DOI: 10.1070/RCR4617

Molybdenum compounds in organic synthesis

Ravil I. Khusnutdinov, Tatyana M. Oshnyakova, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences
prosp. Oktyabrya 141, 450075 Ufa, Russian Federation

The review presents the first analysis and systematic discussion of data published in the last 35 – 40 years on the use of molybdenum compounds and complexes in organic synthesis and catalysis of various ion coordination and radical reactions. Detailed account is given of the key trends in the use of molybdenum complexes as catalysts of alkene epoxidation and oxyketonation, oxidation of sulfur, nitrogen and phosphorus compounds, hydrosilylation of 1,3-dienes, ketones and aldehydes, hydrostannylation of acetylenes and hydrogermylation of norbornadienes. Considerable attention is paid to the description of new reactions and *in situ* generation of highly reactive hypohalites, ROX and HOX, induced by molybdenum complexes and the use of hypohalites in oxidative transformations. Data on the application of molybdenum complexes in well-known reactions are discussed, including Kharasch and Pauson – Khand reactions, allylic alkylation of C-nucleophiles, aminocarbonylation of halo derivatives and oligomerization of cyclic dienes, trienes, alkynes and 1,3-dienes. The last Section of the review considers 'unusual' organic reactions involving molybdenum compounds and complexes.
The bibliography includes 257 references.

Contents

I.	Introduction	128
II.	Epoxidation of alkenes	129
III.	Enantioselective epoxidation of alkenes	133
IV.	Oxyketonation and other oxidation reactions	135
V.	Oxidation of sulfur-, nitrogen- and phosphorus-containing compounds	138
VI.	Generation of ROX and HOX (X = Cl, Br) and oxidative reactions involving them	141
VII.	Transformations of epoxides under the action of molybdenum complexes	143
VIII.	Molybdenum complexes in halogenation reactions	144
IX.	Molybdenum complexes as catalysts of the Kharasch reaction	145
X.	Allylic alkylation of C-nucleophiles	147
XI.	Oligomerization reactions	148
XII.	Catalysis of C – C bond formation	149
XIII.	Molybdenum complexes in hydrosilylation, hydrostannylation and hydrogermylation	151
XIV.	Molybdenum complexes as catalysts of reduction reactions	152
XV.	Catalysis of azirine reactions	154
XVI.	$Mo(CO)_6$-Mediated Pauson – Khand reaction	155
XVII.	Aminocarbonylation of halo derivatives	156
XVIII.	'Unusual' reactions involving molybdenum compounds and complexes	157

I. Introduction

Molybdenum belongs to a unique family of transition metals that are called 'metals of life'; first of all, this is associated with its catalytic properties. The phenomenon of catalysis involving molybdenum compounds has existed since the origin of life. Molybdenum is present in many enzymes, in particular, xanthine oxidase, aldehyde oxidase and sulfite oxidase, which accomplish important physiological redox functions in a human body. They are involved in

R.I.Khusnutdinov. Doctor of Chemical Sciences, Professor, Deputy Director for Science of the IPC RAS.
E-mail: khusnutdinov@anrb.ru
T.M.Oshnyakova. Ph.D (Chemistry), Researcher at the Laboratory of Hydrocarbon Chemistry of the IPC RAS.
E-mail: oshnyakova83@bk.ru
Current research interests of the authors: organic synthesis, metal complex catalysis.

U.M.Dzhemilev. Corresponding Member of the RAS, Director of the IPC RAS, Chairman of Ufa Research Centre of the RAS.
Telephone: +7(347)284 – 2750, e-mail: dzhemilev@anrb.ru
Current research interests: metal complex catalysis in organic and organometallic synthesis, organic chemistry of main group elements, chemistry of strained, cage and cluster compounds, small and unstable molecules.

Received 24 November 2015
Translation: Z.P.Svitanko

© 2017 Russian Academy of Sciences and Turpion Ltd.

the nitrogen exchange *via* regulation of uric acid, promote normalization of tissue respiration and cell growth and play a considerable role in the fat and carbohydrate metabolism.

Apart from participating in the vital biochemical processes, molybdenum compounds and complexes catalyze a multitude of organic reactions.

For instance, heterogeneous Co – Mo catalysts are widely used in hydrotreating of petroleum feedstock to remove sulfur, nitrogen, oxygen and resins.[1] Molybdenum complexes are among the best and versatile catalysts of metathesis.[2,3] Catalysts for nitrogen fixation have been developed on the basis of molybdenum compounds.[4,5] Molybdenum complexes catalyze a variety of oxidation reactions, in particular, alkene epoxidation. The achievements and the progress in the application of molybdenum compounds to catalyze hydrotreating, nitrogen fixation, metathesis and epoxidation are extensively described in subject reviews and monographs.[3,6–14]

A detailed review[6] on the application of molybdenum compounds and complexes in the catalysis was published in 2004. In recent years, small reviews were published, discussing allylic alkylation[15–17] and C – H bond activation reactions[18] catalyzed by molybdenum complexes and the use of MoO_2Cl_2 in catalysis.[13]

As shown by analysis of published data, the range of reactions involving Mo catalysts is being extended every year, and this has stimulated us to attempt to summarize the recent achievements and give a comprehensive view of the catalytic potential of molybdenum compounds.

II. Epoxidation of alkenes

Molybdenum complexes are versatile and efficient catalysts for epoxidation of alkenes of various structures with oxidants such as hydrogen peroxide or alkyl(aryl) hydroperoxides. A large body of data on the use of molybdenum compounds as catalysts of epoxidation of unsaturated compounds has been accumulated in the literature and surveyed in reviews and monographs.[6,12,19–22] Therefore, in this Section of the review, we give a selection of the most interesting earlier results and recent achievements on the use of Mo catalysts in the epoxidation, including chiral reactions.

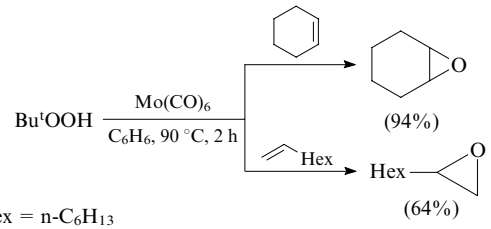
In all of the known studies devoted to alkene epoxidation, starting with the first publications,[23,24] the key challenge is the development of highly efficient, selective and high-performance molybdenum catalysts suitable for oxidation under mild conditions to give products in high yields. Since the first studies, this problem has been mainly solved empirically: by synthesis and testing of the catalytic properties for a variety of molybdenum compounds and complexes that contained known activating ligands used in coordination chemistry and also new ligands, as these ligands have been implemented into practical use.

In the first publications, commercially available and inexpensive molybdenum compounds and complexes were described as epoxidation catalysts, namely, $MoCl_5$, MoO_3, MoB_2, $Mo(CO)_6$, $MoO_2(acac)_2$ (acac is acetylacetonate); $MoCl_5$, $Mo(CO)_6$ and $MoO_2(acac)_2$, which are readily soluble in organic compounds, have been preferred.

One more circumstance is worth noting: in most cases, the catalytic epoxidation in the presence of Mo complexes was studied with a limited range of alkenes.

Sheldon and Van Doorn[25] investigated the liquid-phase epoxidation of cyclohexene and oct-1-ene with *tert*-butyl hydroperoxide in the presence of $Mo(CO)_6$. When the reaction was carried out in benzene for 2 h at 80 °C, the yields of cyclohexene and oct-1-ene epoxides were 94% and 64%, respectively (Scheme 1). Subsequently, using epoxidation of oct-1-ene, researchers found that tetrachloroethane was the solvent of choice for the reaction (90 °C, 2 h, 76% yield of 1,2-epoxyoctane).[26]

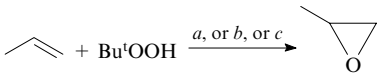
Scheme 1



Hex = n-C_6H_{13}

In a US patent,[27] propylene epoxidation with *tert*-butyl hydroperoxide was accomplished in the presence of $Mo(CO)_6$, MoO_3 or molybdenum naphthenate ($MoNf_3$) at elevated pressure (Scheme 2).

Scheme 2



(*a*) $MoNf_3$, Bu^{t}OH, 80 °C, 2 h (34% yield); (*b*) $Mo(CO)_6$, Bu^{t}OH, 80 °C, 2 h (21%); (*c*) MoO_3, 110 °C, 6 h (42%)

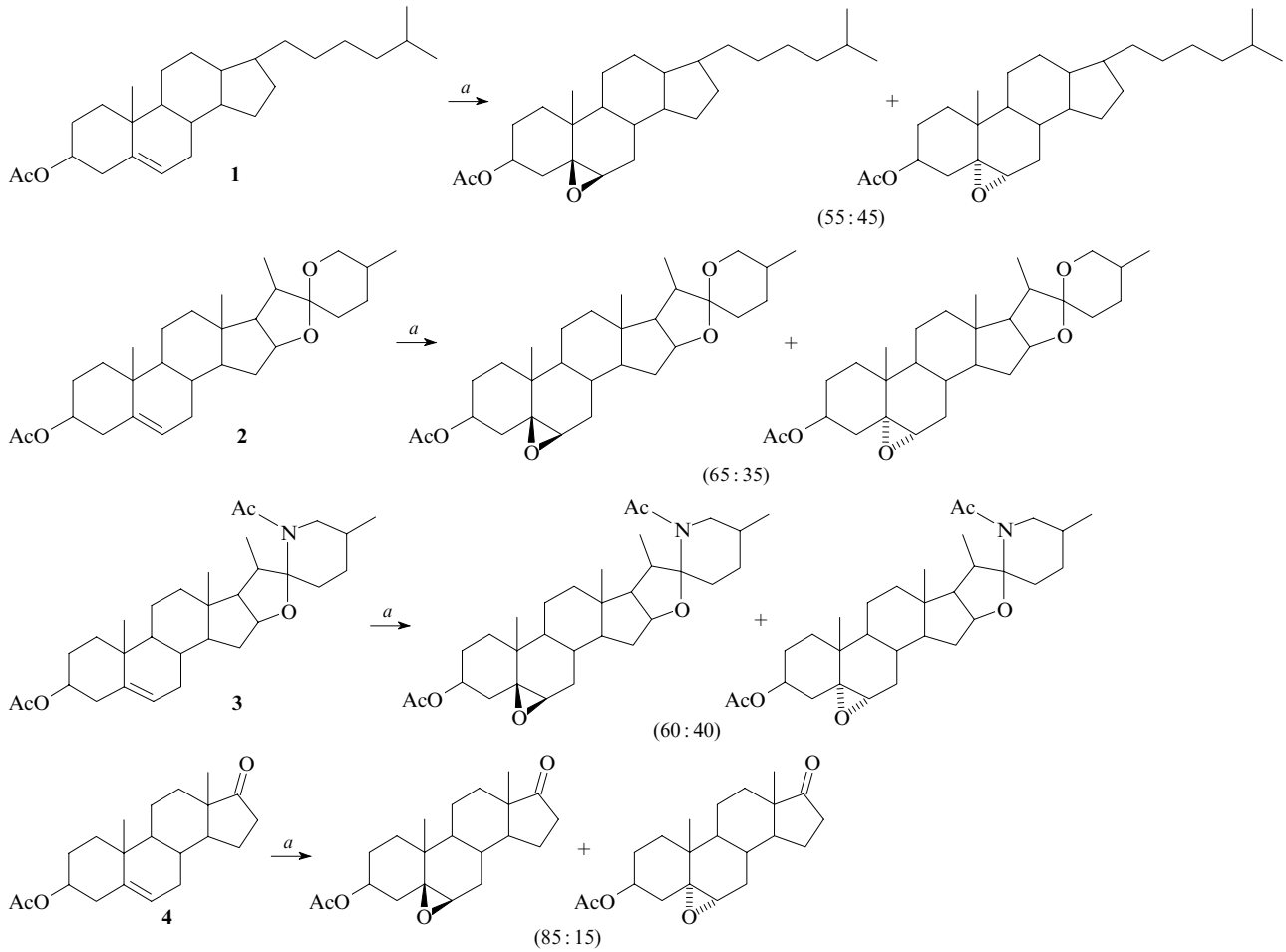
Interesting results were obtained for epoxidation of alkenes of complex structure, namely, Δ^5-steroids and terpenes, on treatment with *tert*-amyl hydroperoxide (Am^{t}OOH) in the presence of molybdenum complexes.[28–30] The stereochemistry of the reaction was found to depend on the structure of the steroid molecule and the substituent nature. Thus the ratios of 5α,6α- and 5β,6β-isomeric epoxides formed from β-acetoxycholest-5-ene (**1**), 3β-acetoxyspirostan-5-ene (**2**), solasodine *O*,*N*-diacetate (**3**) and 3β-acetoxyandrost-5-en-17-one (**4**) are 45 : 55, 35 : 65, 40 : 60 and 15 : 85, respectively. The oxidation of compounds **1** – **4** under these conditions proceeds smoothly (Scheme 3).

Higher stereoselectivity of the reaction towards 5α,6α-oxides (95% – 100%) was achieved when steroids **1** – **4** were epoxidized using the $MoO_5 \cdot$HMPA complex (HMPA is hexamethylphosphoric triamide) taken in a stoichiometric amount.[30,31] As regards epoxidation of terpenes, in particular, α-pinene (**5**), Δ^3- (**6**) and Δ^2-carenes (**7**), they are converted under similar conditions to the corresponding oxides in quantitative yields (Scheme 4).[32]

The possibility of epoxidation of oct-1-ene and 2-ethylallyl ethylacrylate with Bu^{t}OOH in the presence of molybdenum boride was demonstrated (Scheme 5).[33–36]

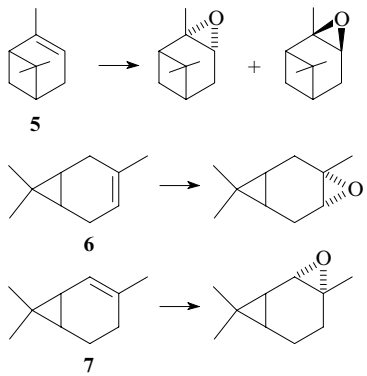
The epoxidation of oleic acid (OA) was studied in the presence of various molybdenum complexes such as $MoNf_3$, $Mo(CO)_6$, $MoO_2(acac)_2$, $H_2[Mo_2O_4(ox)_2(H_2O)_2] \cdot 4H_2O \cdot Me_2CO$ (ox is oxalate), $[MoO_2(SAP)(EtOH)]$ (**8**) (SAP is 2-salicylidenaminophenolate).[37–41] The best results in the OA oxidation with Bu^{t}OOH were attained with the $MoO_2(SAP)(EtOH)$ catalyst, which provided a ~84% yield of 9,10-epoxystearic acid (Scheme 6).[41]

Scheme 3

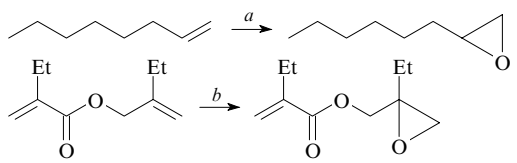


(*a*) Am^{t}OOH, $MoCl_5$, C_6H_6, 60 °C, 2 h

Scheme 4

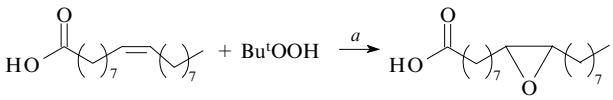


Scheme 5



(*a*) Bu^{t}OOH, MoB_2, 360 K; (*b*) Bu^{t}OOH, MoB_2, 380 K

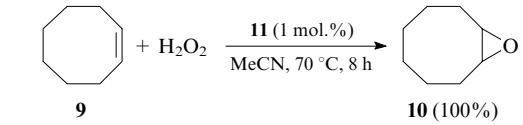
Scheme 6

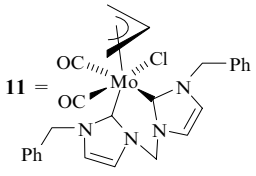


(*a*) **8**, 80 °C, 260 min

High activity and selectivity in the epoxidation of (*Z*)-cyclooctene (**9**) to epoxide **10** under the action of H_2O_2 (**9** : H_2O_2 = 1 : 3) was found for molybdenum complex **11** containing 1,1′-dibenzyl-3,3′-methylenediimidazoline-2,2′-diylidene in the coordination sphere (Scheme 7).[42]

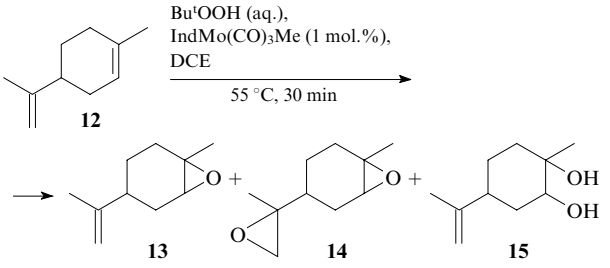
Scheme 7





The epoxidation of alkenes catalyzed by η^5-indenyl molybdenum complexes has a low selectivity.[43] Indeed, the oxidation of dipentene (limonene racemate) (**12**) with Bu^{t}OOH in the presence of $IndMo(CO)_3Me$ (Ind is η^5-indene) gives 1-methyl-4-(1-methylvinyl)-1,2-epoxycyclohexane (**13**) as the major product, which is formed in the highest yield when the reaction is carried out in a water – dichloroethane mixture. Simultaneously, the reaction gives minor amounts of 4-(1,2-epoxyprop-2-yl)-1,2-epoxy-1-methylcyclohexane (**14**) and 1-methyl-4-(1-methylvinyl)cyclohexane-1,2-diol (**15**) (Scheme 8).

Scheme 8



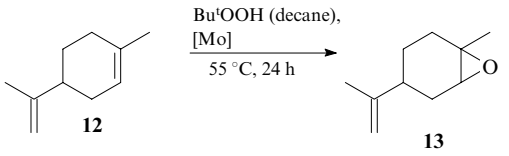
DCE is 1,2-dichloroethane

A broad range of Mo catalysts (complexes **16**, **17a**,**b**, **18a**,**b**, **19**, **20a**,**b**, **21a**,**b** and **22a**,**b**) was used in the epoxidation of dipentene (**12**) with *tert*-butyl hydroperoxide. The polunuclear molybdenum complex $[Mo_8O_{22}(OH)_4$(di-Bu^t-bipy)$_4]$ (**16**) [di-Bu^t-bipy is 4,4′-bis(*tert*-butyl)-2,2′-bipyridine] catalyzes this transformation (55 °C, 24 h) to give epoxide **13** in 79% – 85% yield depending on the presence and nature of the co-solvent.[44] Complex **16** is more active than molybdenum dioxo complexes **17** – **20** (Scheme 9).

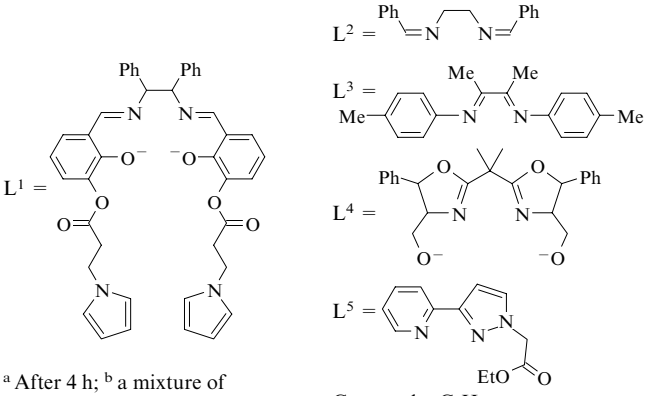
High activity in the epoxidation of alkenes with Bu^{t}OOH was found for molybdenum carbonyl complexes **21a**, **23a**,**b**, **24** – **26**, **27a** – **e**, **28** and **29**, which additionally contain π-allyl,[50] cyclopentadienyl,[50, 53 – 55] nitrile [56] or azomethine [57] ligands in the coordination sphere as well as the Cl^-, Br^-, I^- and RCO_2^- anionic ligands.[50, 55, 56] With these catalysts, epoxidation of (*Z*)-cyclooctene (**9**) can be carried out under relatively mild conditions (24 h at 55 °C). *ansa*-Complexes **27a** – **d**, in which the *ansa*-ligands are bound to the metal in the η^5- and σ-fashions are especially active.[54, 55] With these catalysts, oxidation of (*Z*)-cyclooctene (**9**) proceeds at room temperature in 30 min to give 1,2-epoxycyclooctane (**10**) in a quantitative yield (Scheme 10).

In recent years, ionic liquids (ILs) have been widely used in the synthetic practice. Owing to their strong polarizing effect and mild solvation properties, ILs may serve as templates for metal complex catalysts, thus stabilizing the

Scheme 9



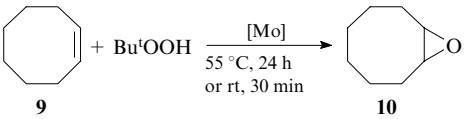
[Mo]	Formula	Yield of **13** (%)	Ref.
16	$Mo_8O_{22}(OH)_4$(di-Bu^t-bipy)$_4$	79 – 85	44
17a	$MoO_2Cl_2(DMF)_2$	39	45
17b	$MoO_2Cl_2(OPEtPh_2)_2$	73	46
18a	$MoO_2Cl_2(H_2L^1)$	65	38
18b	$MoO_2Cl_2L^2$	15 – 20	47
19 [a]	$MoO_2Me_2L^3$	47	48
20a	MoO_2L^4	59	49
20b	MoO_2L^1	50	38
21a	$(\eta^5$-Cp$)Mo(CO)_2(\eta^3$-$C_3H_5)$	70 [b]	50
21b [c]	$(\eta^5$-Cp$)Mo(CO)_3Cl$	21	51
22a	$MoO_2Cl_2L^5$	95	52
22b	$MoO_2(OSiPh_3)_3L^5$	100	52



[a] After 4 h; [b] a mixture of epoxide and diepoxide (1.2 : 1); [c] after 6 h

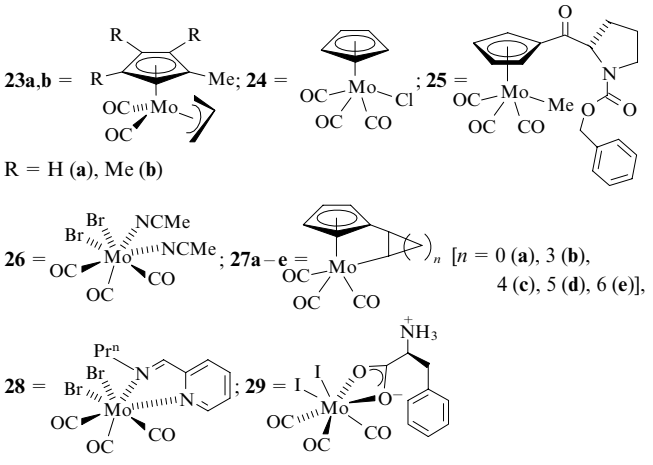
Cp = cyclo-C_5H_5

Scheme 10



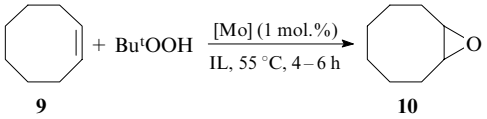
[Mo] = **21a**, **23** – **29**

[Mo]	Yield of **10** (%)	Ref.	[Mo]	Yield of **10** (%)	Ref.
21a	100	50	**27a**	95	54
23a	98	50	**27b**	95	54, 55
23b	81	50	**27c**	95	54
24	100	50	**27d**	96	54
25	97	50, 53	**27e**	30	54
26	100	56	**28**	88	56
			29	13	57



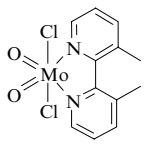
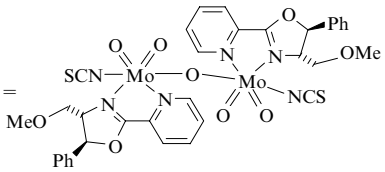
active form of the catalyst and increasing the catalyst performance. These properties of ionic liquids were fully manifested in the epoxidation of (*Z*)-cyclooctene (**9**) in the presence of molybdenum complexes **30** – **32** containing bipyridine and oxazolinylpyridine ligands in the coordination sphere (Scheme 11).[58 – 60]

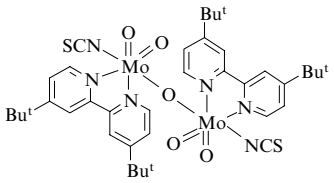
Scheme 11



9 **10**

[Mo]	IL	Yield of **10** (%)	Ref.
30	[bmim]NTf$_2$	31	58
31	[bmim]NTf$_2$	72	59
32	[bmpy]BF$_4$	65	60

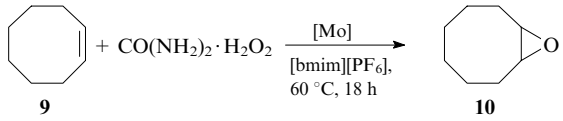
30 = , **31** = 

32 = 

bmim is 1-n-butyl-3-methylimidazolium, bmpy is 1-n-butyl-3-methylpyridinium, Tf = CF_3SO_2

When the 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) ionic liquid is used as the solvent, molybdenum complexes are activated with urea – hydrogen peroxide adduct [$CO(NH_2)_2 \cdot H_2O_2$] towards epoxidation of (*Z*)-cyclooctene (**9**) (Scheme 12).[61]

Scheme 12

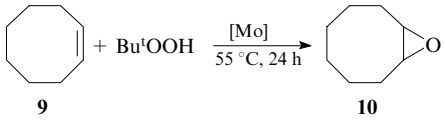


9 **10**

[Mo] : [**9**] : [oxidant] = 0.025 : 1 : 1.5;
[Mo] = $(NH_4)_2Mo_2O_7$ (yield > 90%); MoO_3 (> 90%);
$MoO(O_2)_2$(bipy) (> 90%); $MoO(O_2)_2\left(O\leftarrow N\text{-}Me\right)_2 \cdot H_2O$ (83%)

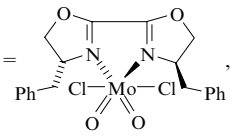
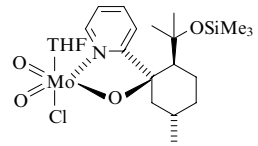
In a number of recent studies, molybdenum oxo, dioxo and peroxo complexes with various ligands have been used as epoxidation catalysts. This choice of complexes was not occasional, as the epoxidation involves strong oxidants (RO_2H, H_2O_2), which are able to convert any molybdenum compounds to oxo, dioxo and peroxo complexes. It is assumed that pre-synthesized molybdenum oxo, dioxo and peroxo complexes would be more active than the low-valence Mo complexes. Scheme 13 summarizes the results of experiments on epoxidation of (*Z*)-cyclooctene (**9**) with *tert*-butyl hydroperoxide in the presence of molybdenum dioxo complexes **18a**, **20a**,**b**, **22a**,**b**, **33**, **34**, **35a**,**b**.[38, 49, 52, 62 – 65]

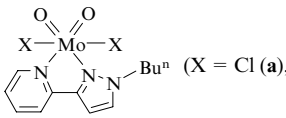
Scheme 13



9 **10**

[Mo] : [**9**] : [Bu^{t}OOH] = 1 : 100 : 160;
[Mo] = **18a** (99% yield), **20a** (65%), **20b** (75%), **22a** (93%), **22b** (90%), **33** (100%), **34** (99%), **35a** (92%), **35b** (88%);

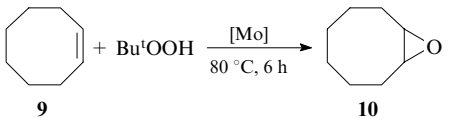
33 = , **34** = 

35a,**b** =  (X = Cl (**a**), $OSiPh_3$ (**b**))

As can be seen from the presented data, the assumption that molybdenum oxo, dioxo and peroxo complexes would be more active in alkene epoxidation proved true only partially. Irrespective of the ligand structure, the catalytic activity of most Mo complexes in the oxidized form does not differ significantly from the activity of known molybdenum compounds, $Mo(CO)_6$, $MoO_2(acac)_2$ and $MoCl_5$.

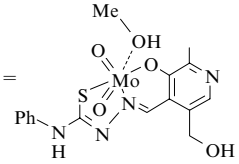
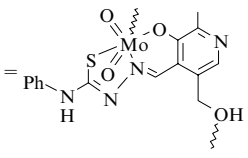
Exceptions are provided by the monomeric (**36**) and polymeric (**37** – **39**) Mo^{VI} pyridoxal thiosemicarbazone complexes, which show high activities in the epoxidation of (*Z*)-cyclooctene (**9**) with an aqueous solution of *tert*-butyl hydroperoxide taken in 0.05 mol.% amount with respect to alkene (Scheme 14).[65]

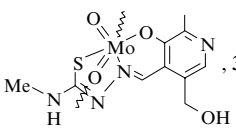
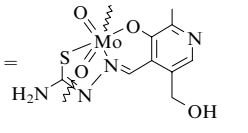
Scheme 14



9 **10**

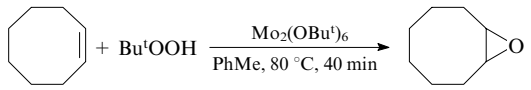
[Mo] : [**9**] : [Bu^{t}OOH] = 1 : 2000 : 4000;
[Mo] = **36** (94% yield), **37** (43%), **38** (65%), **39** (69%);

36 = , **37** = 

38 = , **39** = 

In the series of molybdenum compounds, $Mo_2(OBu^t)_6$ is distinguished by high activity; in the presence of this catalyst, epoxidation of (*Z*)-cyclooctene proceeds at room temperature and is completed within 40 min (Scheme 15).[66]

Scheme 15



9 **10**

[Mo] : [**9**] : [ButOOH] = 1 : 320 : 320

III. Enantioselective epoxidation of alkenes

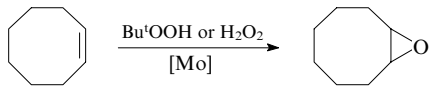
Epoxidation of mono-, di-, tri- and tetrasubstituted alkenes gives rise to a chiral centre. Therefore, it is reasonable that many authors who studied epoxidation of alkenes catalyzed by molybdenum complexes made attempts to perform the epoxide synthesis with asymmetric induction. This problem was solved by the classic method, namely, by using chiral ligands of various nature as parts of Mo-catalyst systems. Traditional oxidants such as H_2O_2, ButOOH, PhCH(Me)OOH and Ph_3COOH were used in these reactions.

For instance, the asymmetric epoxidation of prochiral (*Z*)-cyclooctene (**9**) (Scheme 16), dipentene (**12**) and (*E*)-β-methylstyrene (**40**) with *tert*-butyl hydroperoxide or hydrogen peroxide in chloroform or ethanol was carried out in the presence of *cis*-dioxomolybdenum(VI) complexes **41a**,**b** , **42** with chiral alkoxy(imino) ligands.[67]

Complexes **41b** and **42** exhibited a very high catalytic activity towards epoxidation of (*Z*)-cyclooctene (**9**).[68, 69] Not inferior in activity were the molybdenum complexes $[MoO_2X_2L_2]$ (X = Cl, Br, $OSiPh_3$, Me; L is 3,5-dimethylpyrazole or L_2 is 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 2,2′-bipyrimidine, 4-hexyl-4′-methyl-2,2′-bipyridine, *etc.*)[38, 70 – 74] and $[MoO_2(L,L)_2]$ [(L,L) is 4-ethyl-2-(2-hydroxyphenyl)oxazoline, *etc.*];[75, 76] the epoxide yields in the presence of these complexes were 60% – 100%.[38, 69, 70, 77 – 80]

The enantiodifferentiating ability of complexes **41** and **42** examined in the epoxidation of (*E*)-β-methylstyrene (**40**) proved to be very low (< 2%).[67]

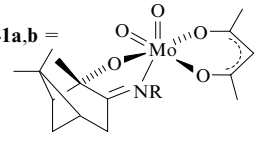
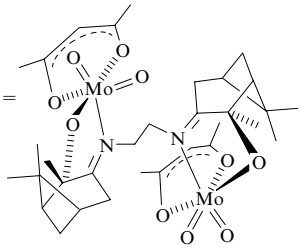
Scheme 16



9 **10**

[Mo] : [**9**] : [oxidant] = 0.01 : 1 : 2, $CHCl_3$ or EtOH, 50 °C

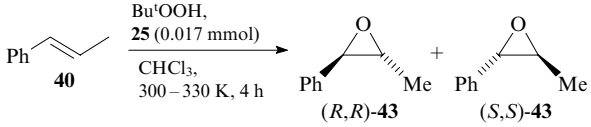
Oxidant	Reaction conditions	Yield of **10** (%)		
		41a	**41b**	**42**
ButOOH	$CHCl_3$, 1 h	73	98	96
H_2O_2	EtOH, 24 h	60	40	36

41a,**b** =  , **42** = 

R = Bn (**a**), pic (**b**); pic is α-picolyl

Chiral molybdenum(VI) complex **25** with the (*N*-benzyloxycarbonylprolyl)cyclopentadienyl ligand catalyzes the epoxidation of (*E*)-β-methylstyrene (**40**) with *tert*-butyl hydroperoxide in chloroform, which proceeds at 300 – 330 K for 4 h and results in a chemical yield of 98%.[53] However, despite the relatively mild conditions, the optical yield of (*R*,*R*)-(+)-[(*R*,*R*)-**43**)] and (*S*,*S*)-(−)-phenylpropylene oxides [(*S*,*S*)-**43**] did not exceed 5%. The decrease in the reaction temperature to 280 K did not increase the enantioselectivity either. Under these conditions, the reaction rate dropped to a minimum. It is noteworthy that complex **25** markedly exceeds in the activity the chiral complexes of the $(\eta^5\text{-Cp})Mo(CO)_3X$ type[81, 82] in similar reactions at 328 K (Scheme 17).

Scheme 17



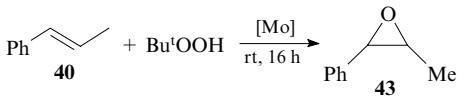
40 (*R*,*R*)-**43** (*S*,*S*)-**43**

(> 98%, *ee* < 5%)

[**25**] : [**40**] : [ButOOH] = 1 : 100 : 200

Molybdenum complexes **44** and **45** containing a chiral cyclopentadienyl ligand with an oxazoline substituent were used as alkene epoxidation catalysts.[83] However, the enantiodifferentiating action of these complexes was found to be weak. Epoxidation of (*E*)-β-methylstyrene (**40**) catalyzed by these complexes at 25 °C for 16 h resulted in the formation of a nearly racemic (*E*)-β-methylstyrene oxide **43** (*ee* ⩽ 5%) (Scheme 18).

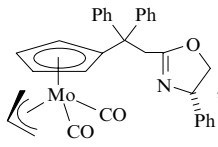
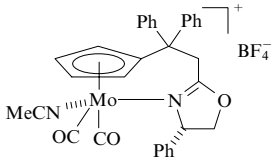
Scheme 18



40 **43**

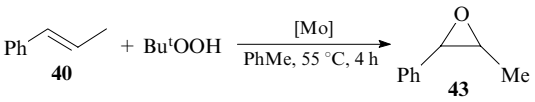
[Mo] : [**40**] : [ButOOH] = 1 : 100 : 200

[Mo]	Yield of **43** (%)	*ee* (%)
44	58	< 5
45	14	< 5

44 =  , **45** = 

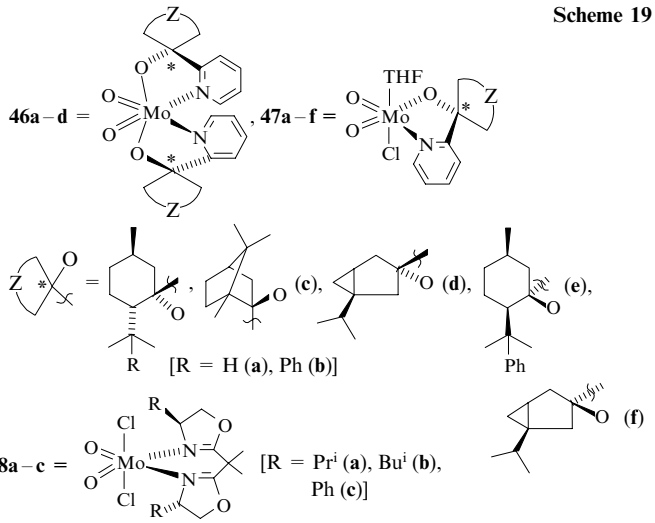
A higher enantioselectivity (*ee* = 23%)[84] was observed in the epoxidation of (*E*)-β-methylstyrene (**40**) with *tert*-butyl hydroperoxide in toluene catalyzed by complexes $MoO_2(L^*)_2$ (**46a** – **d**), $MoO_2Cl(THF)(L^*)$ (**47a** – **f**) and $MoO_2Cl_2(L^{**})$ (**48a** – **c**) (Scheme 19).

In chloroform, the catalytic activity of the $MoO_2(L^*)_2$ (**46**) type complexes was higher; however, the optical yield of epoxides remained low (26%).[68] A moderate catalytic activity and low enantioselectivity were also found for molybdenum complexes in which chiral ligands were represented by 2′-pyridyl-substituted alcohols prepared from carbohydrates — 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose (Δ-**49a** and Λ-**49a**), 2,3 : 5,6-di-*O*-isopropylidene-D-mannofuranose (**49b**) and 1,2 : 3,4-di-*O*-isopropylidene-D-galactopyranose (**49c**) — in the epoxidation of (*E*)-β-methylstyrene (**40**) with ButOOH and cumyl hydroperoxide at



[Mo]	Conversion of **40** (%)	**43**: *ee* (%)	[Mo]	Conversion of **40** (%)	**43**: *ee* (%)
46a	47	5 (*S*,*S*)	**47c**	59	12 (*S*,*S*)
46b	46	1 (*S*,*S*)	**47d**	69	18 (*S*,*S*)
46c	23	3 (*S*,*S*)	**47e**	75	16 (*R*,*R*)
46d	51	23 (*S*,*S*)	**47f**	81	11 (*R*,*R*)
47a	76	2 (*S*,*S*)	**48a**	59	–
47b	66	2 (*S*,*S*)	**48b**	72	–
			48c	86	–

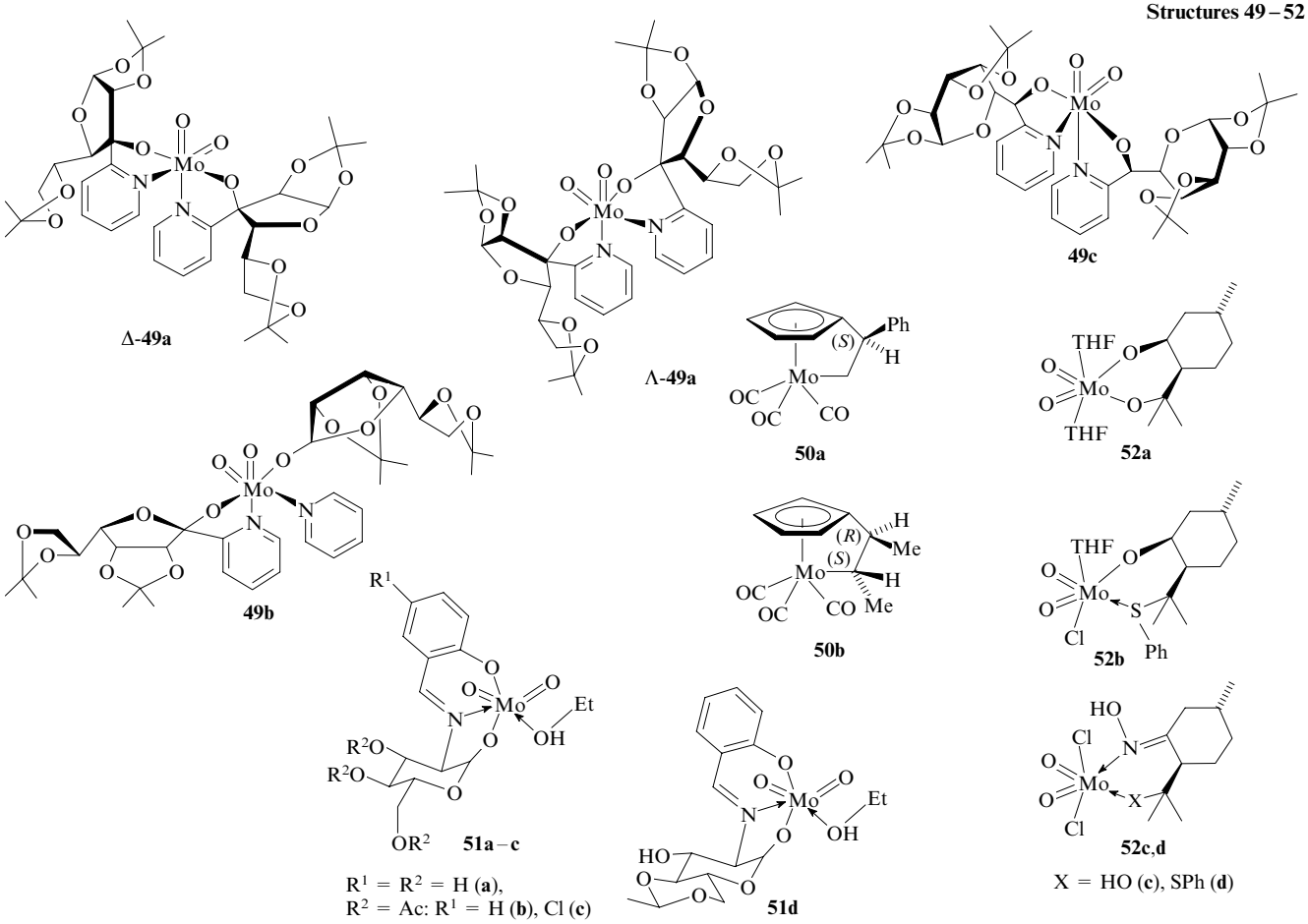
Scheme 19



70 °C for 6 h.[85] A low enantioselectivity (13% – 20%) in the epoxidation of (*E*)-β-methylstyrene with ButOOH was found for *ansa*-η5-cyclopentadienyl molybdenum complexes: (*S*)-[Mo(η5-$C_5H_4CHPhCH_2$)$(CO)_3$] (**50a**) and (*R*,*S*)-[Mo(η5-$C_5H_4CHMeCHMe$)$(CO)_3$] (**50b**)[81] and molybdenum complexes containing chiral Schiff bases with carbohydrate substituents, *cis*-diols and bidentate O,N- (**51a – d**, **52c**),[86] O,O- (**52a**), O,S- (**52b**) and N,S-ligands (**52d**).[69]

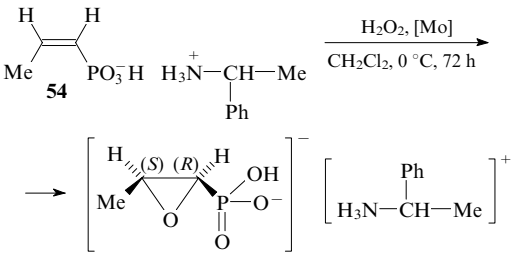
A rather high enantioselectivity (80% *ee*) is observed in the synthesis of a salt of (1*R*,2*S*)-(–)-1,2-epoxypropylphosphonic acid (fosfomycin) (**53**) *via* epoxidation of a salt of (*Z*)-propen-1-ylphosphonic acid (**54**) with hydrogen peroxide in the presence of chiral molybdenum complexes: MoO_2(salen′) (**55**) (salen′ is *N*,*N*′-ethylene-1,2-diphenylbis(3-*tert*-butyl-5-methylsalicylimine), MoO_2[(+)-campy]$_2$ (**56**) [(+)-campy is (1*R*,2*R*,4*S*)-1,7,7-trimethyl-2-(2-pyridyl)bicyclo[2.2.1]heptan-2-ol], MoO_2[(–)-fenpy]$_2$ (**57**) [(–)-fenpy is (1*R*,2*R*,4*S*)-1,3,3-trimethyl-2-(2-pyridinyl)bicyclo[2.2.1]heptan-2-ol].[87] It was found that the enantioselectivity of the reactions in the presence of Mo complexes **55** – **57** depends substantially not only on the nature and

Structures 49 – 52



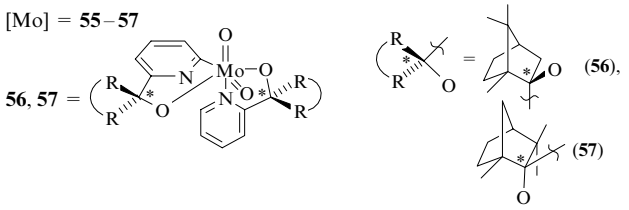
structure of the chiral ligand, but also on the temperature and solvent nature. The best results were obtained by using complex **56** in CH_2Cl_2 (0 °C, 72 h). Under these conditions, the yield of fosfomycin salt **53** was 100% and the optical purity was 80% (Scheme 20).

Scheme 20



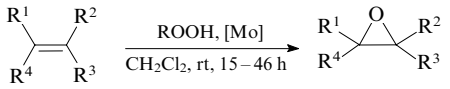
53 (100%)

([Mo] = **56**, 80% *ee*, [Mo] = **57**, 77% *ee*)

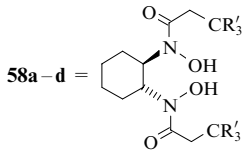


The highest enantioselectivity (95%) was achieved in the epoxidation of mono-, di- and trisubstituted alkenes with *tert*-butyl hydroperoxide, cumyl hydroperoxide ($PhCMe_2OOH$) and trityl hydroperoxide (Ph_3COOH) in the presence of $MoO_2(acac)_2$ activated by chiral bis-hydroxamic acid (BHA) derivatives **58a** – **d**.[88] The advantages of the $MoO(acac)_2$ – BHA catalyst system are high stability in air, the ease of preparation of complexes and versatile activity, which allows performing the reaction with substituted alkenes of complex structure (Scheme 21).

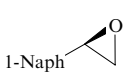
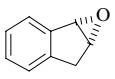
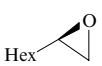
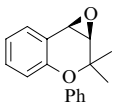
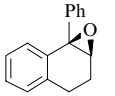
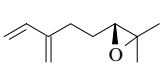
Scheme 21



[Mo] = $MoO_2(acac)_2$ – BHA (1 : 1); [Mo] : [alkene] : [ROOH] = 1 : 50 : 75



R′ = 4-XC_6H_4 [X = Me (**a**), Pr^i (**b**), Bu^t (**c**), Ad (**d**)]

Epoxide	Ligand	ROOH	Time /h	Epoxide yield (%)	*ee* (%)	Epoxide	Ligand	ROOH	Time /h	Epoxide yield (%)	*ee* (%)
	**58b**	Ph_3COOH	20	60	90 (*S*,*R*)		**58c**	$PhCMe_2OOH$	40	95	85 (*R*)
	**58b**	Ph_3COOH	18	98	95 (*S*,*R*)		**58c**	$PhCMe_2OOH$	36	84	82 (*R*)
	**58a**	Ph_3COOH	20	94	92 (*S*,*R*)		**58c**	$PhCMe_2OOH$	40	92	50 (*R*)
	**58c**	Bu^tOOH	20	92	96 (*R*,*R*)		**58c**	$PhCMe_2OOH$	40	95	85 (*R*)
	**58c**	Bu^tOOH	36	44	62 (*S*,*R*)		**58d**	$PhCMe_2OOH$	42	82	76 (*R*)

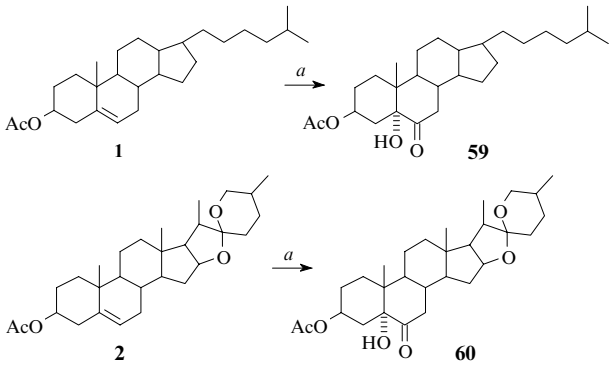
Naph is naphthyl, Cy is cyclohexyl, Ad is adamantyl

IV. Oxyketonation and other oxidation reactions

A vivid example of the extensive synthetic potential of molybdenum complexes in oxidative transformations is the direct oxidation of trisubstituted alkenes to α-hydroxy ketones on treatment with alkyl hydroperoxides.[28,89]

This new type of alkene transformations, which is called oxyketonation, has been studied in detail in relation to steroids and terpenes.[28,89] It is noteworthy that the use of excess oxidant is a necessary condition for the reaction of trisubstituted alkenes to proceed towards oxyketonation. Indeed, the oxidation of cholesterol (**1**) and diosgenin (**2**) acetates on treatment with Am^tOOH (2 – 8 equiv.) gives 5α-hydroxy 6-ketones **59** and **60** in 85% – 90% yields. As side products, 5α,6β-diols are formed (5% – 10% yield) (Scheme 22).

Scheme 22

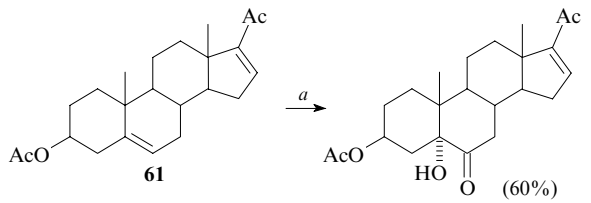


(*a*) Am^tOOH, $MoCl_5$, C_6H_6, 60 °C, 2 h

The oxidation does not affect the electron-deficient double bond. For example, Δ^{16}-dehydropregnenolone acetate (**61**) is oxidized at the Δ^5 bond, while the Δ^{16} double

bond adjacent to the keto group remains intact (Scheme 23).[89]

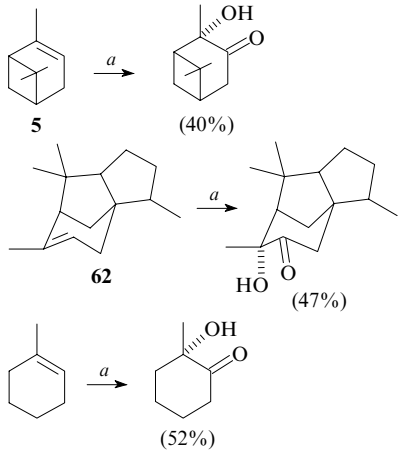
Scheme 23



(*a*) Am^{t}OH, $MoCl_5$, 60 °C, 2 h

Oxyketonation of terpenes with a trisubstituted double bond, α-pinene (**5**), α-cedrene (**62**) and 1-methylcyclohexene, has been reported.[89] The reactions with these substrates were catalyzed by $Mo(CO)_6$ (Scheme 24).

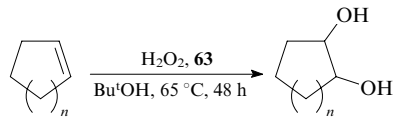
Scheme 24



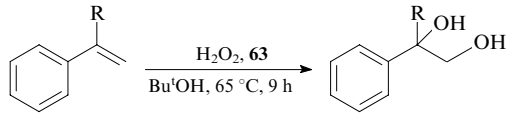
(*a*) Am^{t}OOH, $Mo(CO)_6$, C_6H_6, 80 °C, 2 h

The molybdenum acetylenide complex (η^5-Cp)$Mo(CO)_3$(C≡CPh) (**63**) catalyzes the selective *cis*-dihydroxylation of a number of alkenes with H_2O_2. The highest performance of the catalyst is observed in *tert*-butyl alcohol (Scheme 25).[90]

Scheme 25



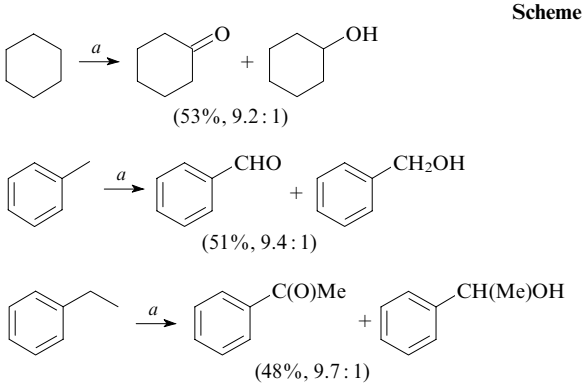
n = 1 (82% yield), 2 (86%)



R = H (82% yield), Me (58%)

The molybdenum oxo(peroxo) complex $MoO(O_2)$(phox)$_2$ (**64**) [phox is 2-(2-hydroxyphenyl)oxazoline] catalyzes the oxidation of cyclohexane, toluene and ethylbenzene with hydrogen peroxide (Scheme 26).[91]

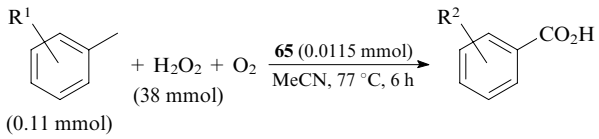
Scheme 26



(*a*) H_2O_2, **64** (2 mol.%), rt, 12 h

The molybdenum complex with the 8-hydroxyquinoline ligand, $MoO(O_2)(QO)_2$ (**65**) (QO is 8-quinolinolate anion) is an efficient catalyst for the side-chain oxidation of methylbenzenes (toluene and *o*- and *p*-xylenes) with the $H_2O_2-O_2$ system to give the corresponding carboxylic acids (Scheme 27).[92]

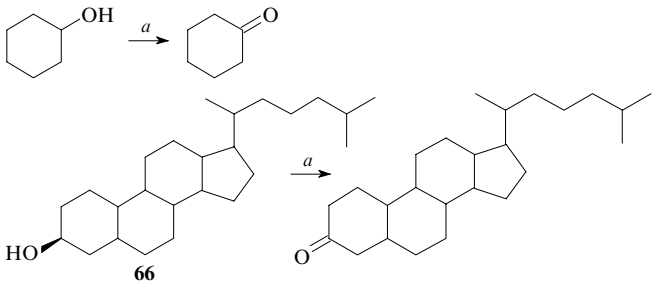
Scheme 27



R^1	R^2	Yield (%)
H	H	95
2-Me	2-CO_2H	76
4-Me	4-Me	88

The Am^{t}OOH – $MoCl_5$ reagent actively oxidizes secondary alcohols to ketones. In the presence of $MoCl_5$, cyclohexanol and 3-β-cholestanol (**66**) are oxidized with *tert*-amyl hydroperoxide to give ketones in 80% yield (Scheme 28).[93]

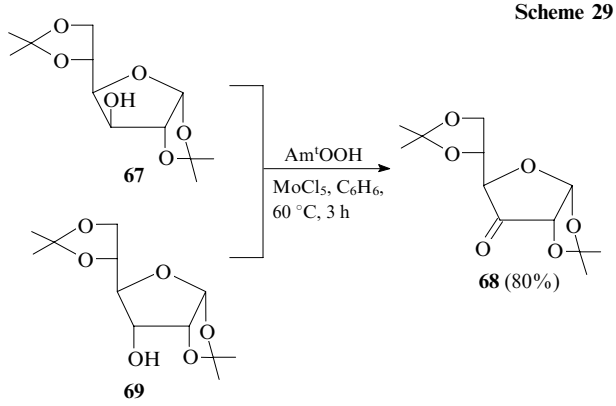
Scheme 28



(*a*) Am^{t}OOH, $MoCl_5$, C_6H_6, 60 – 80 °C, 3 – 20 h;
[alcohol] : [Am^{t}OOH] = 1 : 3

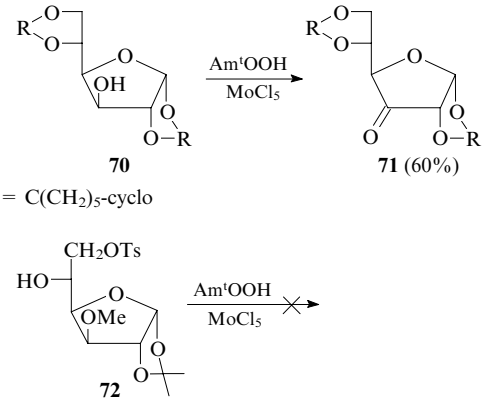
An important application of the Am^{t}OOH – $MoCl_5$ reagent is the selective oxidation of carbohydrates to keto sugars. Treatment of D-glucofuranose diacetonide (**67**) with excess Am^{t}OOH in the presence of $MoCl_5$ in boiling benzene gives D-ribohexofuranose diacetonide **68**. Allofuranose diacetonide **69** is oxidized to give ketone **68** in an equally high yield (Scheme 29).[93, 94]

Scheme 29



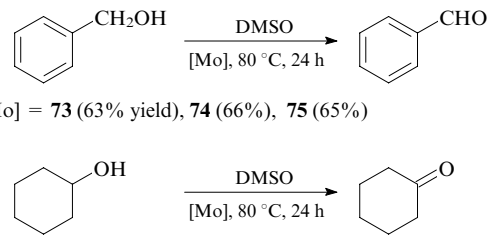
The degree of oxidation of carbohydrates depends on the structure and nature of protecting groups.[93,94] For example, the conversion of dicyclohexylideneglucose (**70**) to the corresponding keto sugar **71** is 60%. The oxidation of 1,2-isopropylidene-3-*O*-methyl-6-*O*-tosylglucofuranose (**72**) does not proceed at all, the initial compound being recovered unchanged (Scheme 30).

Scheme 30



Molybdenum dioxo complexes with isothiocyanate and bipyridine ligands, $(PPh_4)_2[Mo^{VI}O_2(NCS)_4]$ (**73**), $Mo^{VI}O_2(NCS)_2$(di-Bu^t-bipy) (**74**) and $Mo_2{}^{VI}O_5(NCS)_2$(di-Bu^t-bipy)$_2$ (**75**), catalyze the oxidation of benzyl alcohol with dimethyl sulfoxide to give benzaldehyde.[60] Cyclohexanol is converted under similar conditions to cyclohexanone, but in a low yield (Scheme 31).

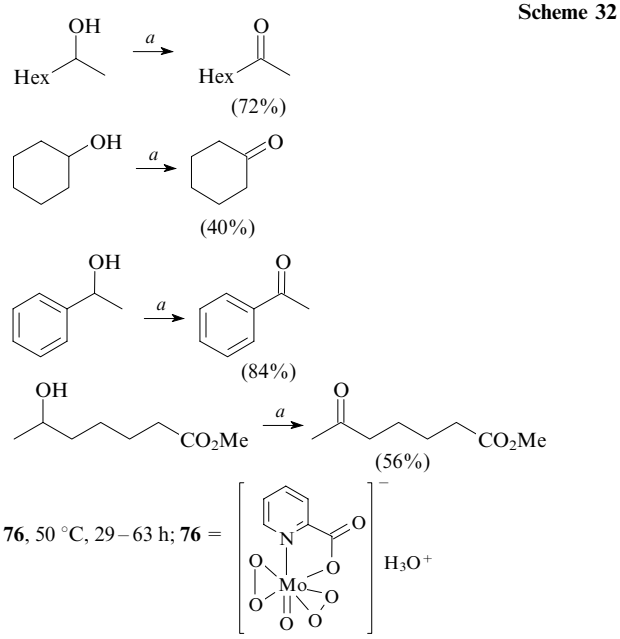
Scheme 31



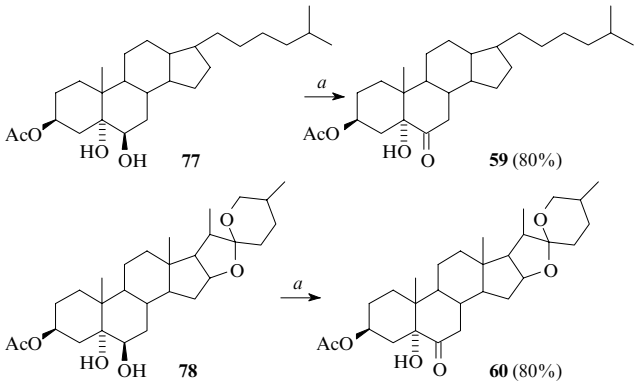
Molybdenum peroxo complex **76** stabilized by a bidentate ligand, picolinic acid, catalyzes the oxidation of secondary alcohols (Scheme 32).[95]

The Am^{t}OOH – $MoCl_5$ reagent smoothly oxidizes 1,2-diols to α-hydroxy ketones.[93,94] For example, secondary-tertiary α-glycols — 3β-acetoxycholestane-5α,6β-diol (**77**) and 3β-acetoxyspirostane-5α,6β-diol (**78**) — are oxidized at position 6 to give the corresponding 5α-hydroxy ketones **59** and **60** in high yields (Scheme 33).

Scheme 32



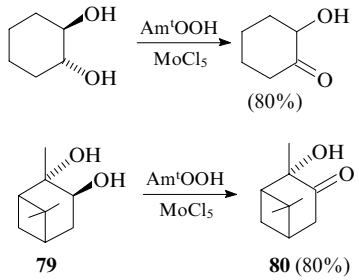
Scheme 33



(*a*) Am^{t}OOH, $MoCl_5$, 60 – 80 °C

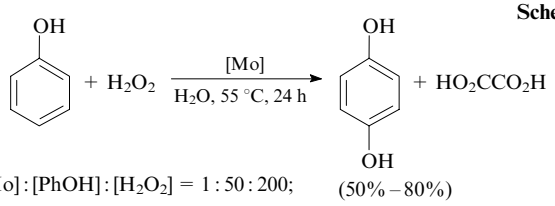
Under similar conditions, *trans*-cyclohexane-1,2-diol and pinane-2α,3β-diol (**79**) are easily oxidized to give 2-hydroxycyclohexanone and 2-hydroxy-3-pinanone (hydroxypinocamphone, **80**), respectively (Scheme 34).

Scheme 34

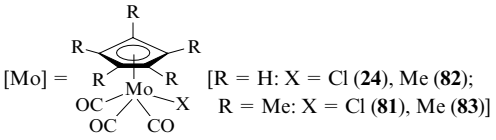


Molybdenum cyclopentadienyl complexes **24** and **81** – **83** catalyze the phenol oxidation to hydroquinone with hydrogen peroxide in water. Oxalic acid is formed as a side

Scheme 35



[Mo] : [PhOH] : [H_2O_2] = 1 : 50 : 200; (50% – 80%)



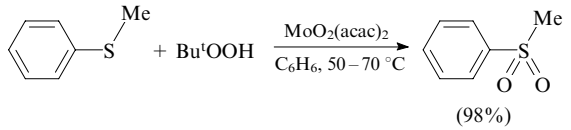
[R = H: X = Cl (**24**), Me (**82**); R = Me: X = Cl (**81**), Me (**83**)]

product (Scheme 35).[96] Complexes **24** and **83** were most active in this reaction. In the absence of catalysts, phenol is oxidized to *p*-benzoquinone and *o*-benzoquinone.

V. Oxidation of sulfur-, nitrogen- and phosphorus-containing compounds

Quite a few studies are devoted to the oxidation of sulfur-containing derivatives with hydroperoxides in the presence of Mo catalysts. An early paper[97] published in 1966 was concerned with the oxidation of thioanisole with *tert*-butyl hydroperoxide in the presence of the $MoO_2(acac)_2$ catalyst (Scheme 36).

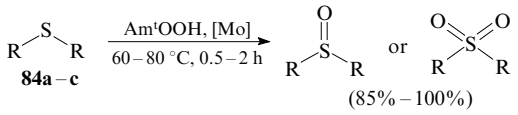
Scheme 36



(98%)

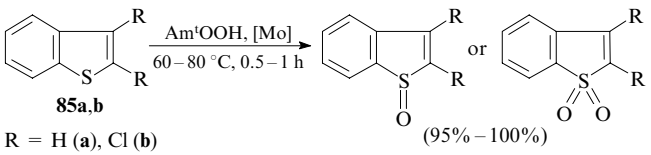
A series of studies of Tolstikov *et al.*[98,99] described the $MoCl_5$- and $Mo(CO)_6$-catalyzed oxidation of alicyclic sulfides **84a – c** and sulfur-containing aromatic heterocycles

Scheme 37



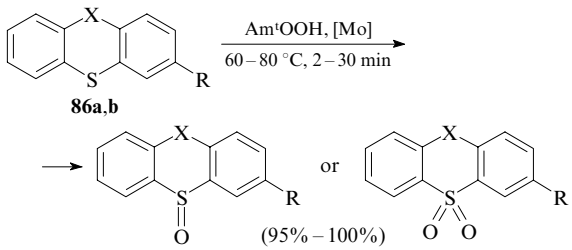
(85% – 100%)

R = Cy (**a**), 2-Cl-cyclo-C_6H_{10} (**b**), 2-AcO-cyclo-C_6H_{10} (**c**)



(95% – 100%)

R = H (**a**), Cl (**b**)



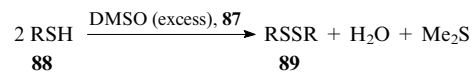
(95% – 100%)

X = O, R = H (**a**); X = NH, R = Cl (**b**);
[Mo] : [sulfide] : [AmtOOH] = (0.5 – 1) : 100 : 100 or (0.5 – 1) : 100 : (200 – 300); [Mo] = $MoCl_5$, $Mo(CO)_6$

85a,**b** and **86a**,**b** with *tert*-amyl hydroperoxide. By varying the hydroperoxide concentration, one can control the degree of oxidation of sulfides to the corresponding sulfoxides and sulfones, which are formed in nearly quantitative yields (Scheme 37).

The molybdenum dioxo complex $MoO_2Cl_2(DMSO)_2$ (**87**) catalyzes the oxidation of thiols **88** to disulfides **89** with dimethyl sulfoxide, which is taken in excess and functions simultaneously as the solvent (Scheme 38).[100]

Scheme 38

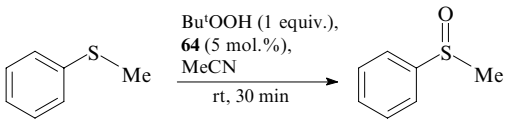


R	Conditions	Yield of **89** (%)	R	Conditions	Yield of **89** (%)
Ph	*a*	98	2-Py	*a*	89
2-ClC_6H_4	*a*	94	2-$OHCC_6H_4$	*a*	91
4-ClC_6H_4	*a*	95	2-$Me_2(HO)CC_6H_4$	*a*	98
4-MeC_6H_4	*a*	96	Bn	*b*	94
4-$MeOC_6H_4$	*a*	95	n-C_8H_{17}	*b*	87
2-$H_2NC_6H_4$	*a*	91	n-$C_{12}H_{25}$	*b*	86
2-$HO_2CC_6H_4$	*a*	90	Bu^t	*b*	85

(*a*) **87** (1 mol.%), rt, 30 min; (*b*) **87** (5 mol.%), 70 °C, 6 h; Py is pyridyl.

The molybdenum oxo peroxo complex $MoO(O_2)(phox)_2$ (**64**) catalyzes the oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide under the action of *tert*-butyl hydroperoxide[101] (Scheme 39).

Scheme 39



(89%)

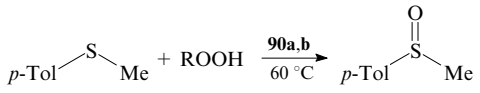
Methyl *p*-tolyl sulfide can be oxidized to the sulfoxide on treatment with hydrogen peroxide or *tert*-butyl and cumyl hydroperoxides in the presence of molybdenum complexes **90a**,**b** containing *tert*-butylphenolamine ligands in the coordination sphere. The best results were obtained with the use of H_2O_2 (Scheme 40).[102]

The molybdenum cyclopentadienyl complexes (η^5-Cp)$Mo(CO)_3Cl$ (**24**), (η^5-Cp*)$Mo(CO)_3Cl$ (Cp* = C_5Me_5) (**81**) and (η^5-Cp)MoO_2Cl (**91**) catalyze the oxidation of sulfides to sulfoxides and sulfones on treatment with hydrogen peroxide.[103] The reaction proceeds at room temperature over a period of 1 – 5 h (Scheme 41).

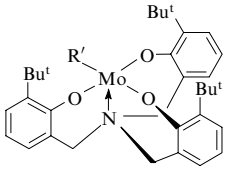
MoO_2Cl_2 is a fairly active catalyst for the oxidation of disulfides to sulfoxides with H_2O_2.[104] The oxidation of disulfides affords sulfoxides, no disulfoxides or sulfones being formed even with excess hydrogen peroxide (Scheme 42).

Molybdenum(V) complexes with chiral β-cyclodextrin containing 2,3- and 2,4-dihydroxybenzyl ligands show high activity towards oxidation of aromatic sulfides with hydroperoxides. The reaction has high enantioselectivity, the product configuration depending on the number and structure of the Mo complex.[105] The oxidation of alkyl aryl sulfides with trityl hydroperoxide catalyzed by the

Scheme 40



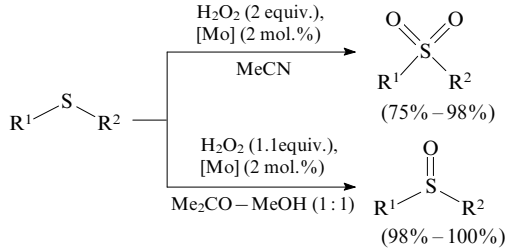
[*p*-TolSMe] : [ROOH] : [Mo] = 1 : 1 : 0.01;

90a,**b** =  [R′ = Cl (**a**), OMe (**b**)]

R	[Mo]	Solvent	$t_{1/2}$ /min [a]	Yield of *p*-TolS(O)Me (%)
$PhCMe_2$	**90a**	$CDCl_3$	47	90
$PhCMe_2$	**90b**	$CDCl_3$	60	91
Bu^t	**90a**	$CDCl_3$	30	83
Bu^t	**90b**	$CDCl_3$	135	65
H	**90a**	CD_3OD	12	99
H	**90b**	CD_3OD	20	99

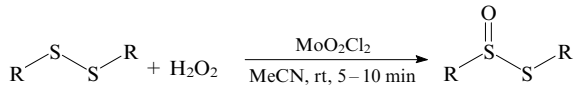
[a] Half-life of ROOH.

Scheme 41



$R^1 = R^2 = Ph$, Bu^n; $R^1 = Me$: $R^2 = 4\text{-}MeOC_6H_4$, $4\text{-}O_2NC_6N_4$, $4\text{-}ClC_6H_4$

Scheme 42

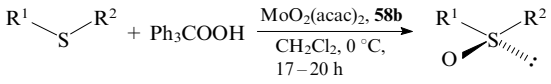


R = Bu^t, Ph

$MoO_2(acac)_2$ – **58b** system occurs with high conversion of the starting compound and high enantioselectivity (Scheme 43).[106]

Dialkyl, alkyl aryl and diaryl sulfides, selenides, tellurides, sulfoxides, selenoxides and telluroxides are oxidized with molybdenum peroxide in THF at 65 °C to the corresponding sulfones, selenones and tellurones (Scheme 44).[107]

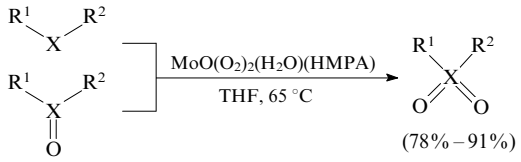
Scheme 43



R^1	R^2	Yield of sulfoxide (%)	*ee* (%)
Ph	Me	81	79 (*S*)
$4\text{-}MeC_6H_4$	Me	75	81 (*S*)
$2\text{-}MeC_6H_4$	Me	76	75 (*S*)
Ph	Et	81	82 (*S*)
Ph	Pr^i	66	62 (*R*)

The authors noted that the oxidation of selenides, sulfides and tellurides proceeds *via* the formation of selenoxides, sulfoxides and telluroxides, respectively; therefore, the oxidation of Se, S and Te oxides requires a lesser amount of the molybdenum complex.

Scheme 44

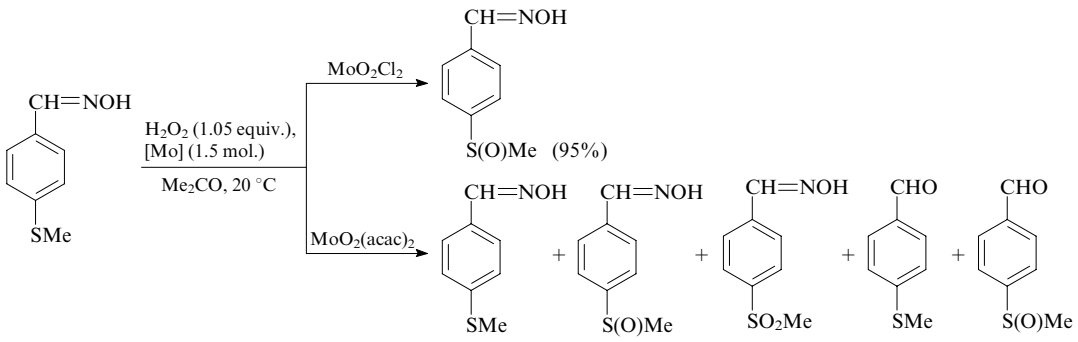


[substrate] : [Mo] = 1 : 1.5 or 1 : 3 (mol.); X = S, Se, Te;
R^1, R^2 = Pr^n, Bu^n, $n\text{-}C_{10}H_{21}$, Ph, $4\text{-}MeC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}ClC_6H_4$, $3\text{-}ClC_6H_4$, $2\text{-}ClC_6H_4$

Hydrogen peroxide oxidizes 4-(methylthio)benzaldehyde oxime in the presence of MoO_2Cl_2 to give the corresponding sulfoxide, while in the presence of $MoO_2(acac)_2$, a complex mixture of the products is formed as a result of oxidation of the oxime group to the aldehyde one (Scheme 45).[104]

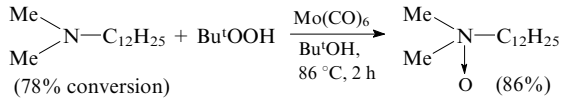
Molybdenum compounds catalyze the oxidation of tertiary amines to N-oxides on treatment with hydroperoxides (Scheme 46).[108]

Scheme 45



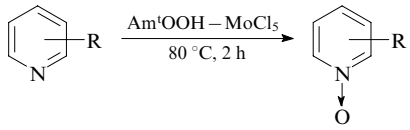
(72% conversion; 9 : 1.7 : 1 : 20 : 1)

Scheme 46

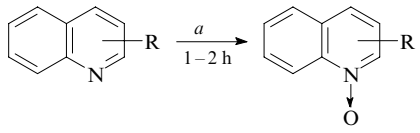


The $Am^tOOH-MoCl_5$ reagent smoothly oxidizes aza heterocycles to N-oxides in boiling benzene.[93, 109] The yields of the corresponding N-oxides depend on the structure of the aza heterocycle and the nature of the substituent and reach 100%. Of considerable interest is the oxidation of phenazine, which is converted to the dioxide in a high yield (Scheme 47).

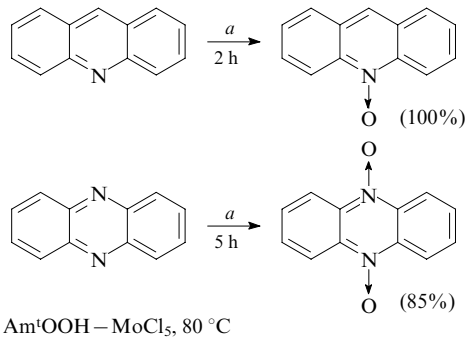
Scheme 47



R = H (100% yield), 2-Me (100%), 3-Me (100%), 2-Ph (95%), 3-CN (80%), 3-Br (90%), 3-CO_2Me (90%), 3-C(O)NH_2 (50%), 4-(4-Py) (80% of dioxide)



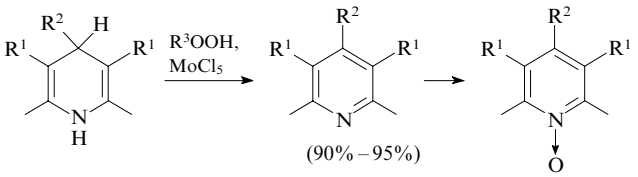
R = H (100% yield), 2-Me (100%), 2-CO_2Me (90%)



(*a*) $Am^tOOH-MoCl_5$, 80 °C

Tolstikov *et al.*[110] performed dehydrogenation of a number of 1,4-dihydropyridines on treatment with *tert*-butyl, *tert*-amyl and cumyl hydroperoxides in the presence of $MoCl_5$. The reaction does not stop after the formation of pyridines, but continues, resulting in pyridine *N*-oxides as the final products (Scheme 48).

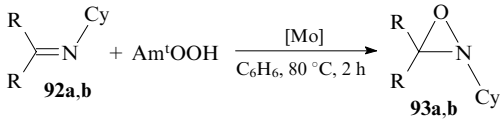
Scheme 48



$R^1 = CO_2Me$, $R^2 = H$; $R^1 = CO_2Et$: R^2 = H, Et, Pr^n, Ph, 3,4-$(MeO)_2C_6H_3$; $R^3 = Bu^t$, Am^t, $PhCMe_2$

The oxidation of Schiff bases **92a**,**b** with Am^tOOH in the presence of $MoCl_5$ and $Mo(CO)_6$ affords oxaziridines **93a**,**b** in 85% – 90% yields (Scheme 49).[111]

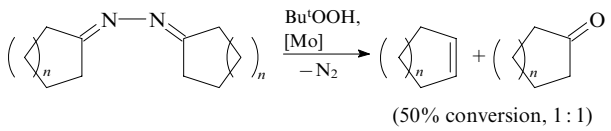
Scheme 49



R = Me (**a**, 85% yield); R – R = $(CH_2)_5$ (**b**, 90%)

Dzhemilev *et al.*[112] described an original method for the synthesis of alkenes from ketones *via* ketazines, which are oxidized with *tert*-butyl hydroperoxide in the presence of $MoCl_5$ or $Mo(CO)_6$ as catalysts. The reaction is accompanied by nitrogen evolution and gives an alkene and a ketone (Scheme 50).

Scheme 50



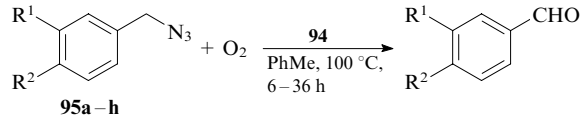
(50% conversion, 1 : 1)

[Mo] = $MoCl_5$ or $Mo(CO)_6$, C_6H_6, 80 °C, 1 h; n = 1 – 4

According to authors' assumption, the reaction proceeds *via* the formation of a diazo compound.

The molybdenum xanthate complex $MoO_2(Et_2NCS_2)_2$ (**94**) behaved as an efficient catalyst in the aerobic selective oxidation of benzyl azides to aldehydes.[113] The reaction patterns were investigated considering the oxidation of *p*-methoxybenzyl azide (**95a**) as a model substrate. The reaction is general; it can also be carried out for other benzyl azides **95b** – **h** (Scheme 51).

Scheme 51



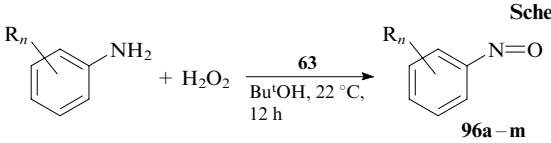
R^1 = H: R^2 = OMe (**a**, 86% yield), H (**b**, 78%), Cl (**c**, 61%), CH(OH)Me (**d**, 88%), Me (**e**, 95%), Ac (**f**, 48%); $R^1 = R^2$ = OMe (**g**, 82%); R^1 = OMe, R^2 = OAll (**h**, 92%)

Hydrogen peroxide oxidizes aniline and its derivatives in the presence of molybdenum complexes to give nitroso compounds **96a** – **m**.[114] The highest yield of nitroso compounds is observed in a *tert*-butyl alcohol solution. The turnover number (TON) for the catalyst $(\eta^5\text{-Cp})Mo(CO)_3(C{\equiv}CPh)$ (**63**) in this reaction was 470, which is much higher than that for $MoO(O_2)(H_2O)(HMPA)$ (TON ≈ 9)[115, 116] or $MoO_2(acac)_2$ (TON < 10) (Scheme 52).[117]

The high oxidative ability of the $Am^tOOH-MoCl_5$ reagent is well illustrated by the oxidation of *N*-nitrosamines **97** and **98a**,**b** to give nitramines **99** and **100a**,**b** (Scheme 53).[93, 109, 111]

Molybdenum dioxo complexes such as $MoO_2X_2(DMSO)_2$ (X = F, Cl, Br) catalyze the oxidation of triphenylphosphine (Scheme 54).[118] Fairly high activity in the PPh_3 oxidation was found for $MoO_2(dtc)_2$ (dtc is diethyldithiocarbamate). However, it is unstable in DMSO and decomposes to unidentified compounds, which are more active than the initial complex.

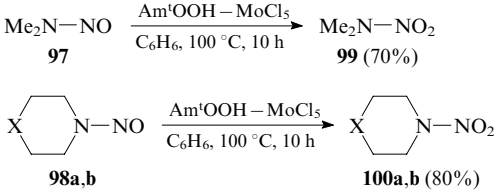
Scheme 52



96a – m

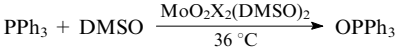
Compound **96**	R_n	Conversion (%)	Selectivity (%)
a	H	97	97
b	4-Me	100	99
c	2,6-Me_2	75	99
d	4-OMe	83	97
e	2-NH_2	77	98
f	4-NH_2	84	99
g	2-OH	73	98
h	4-OH	75	98
i	2-Cl	60	96
j	3-Cl	72	99
k	2-F	79	79
l	3-F	80	74
m	4-NO_2	85	95

Scheme 53



X = CH_2 (**a**), O (**b**)

Scheme 54

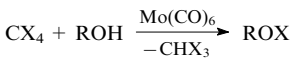


Catalyst	Time /min	Conversion of PPh_3 (%)
$MoO_2X_2(DMSO)_2$		
X = Cl	60	95
X = Br	200	90
X = F	inactive	–
$MoO_2(dtc)_2$	230	90

VI. Generation of ROX and HOX (X = Cl, Br) and oxidative reactions involving them

Recently, it was found that molybdenum compounds and complexes catalyze an unusual reaction of alcohols with halomethanes, resulting in the formation of highly reactive molecules, alkyl hypohalites (Scheme 55).[119, 120] For example, the reaction of CCl_4 with methanol in the presence of catalytic amounts of $Mo(CO)_6$ (150 °C) yields methyl hypochlorite, the concentration of which in the reaction mixture is 3.5 mg ml^{-1} after 20 min.[121]

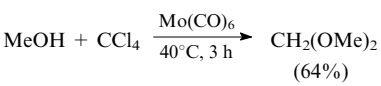
Scheme 55



X = Cl, Br

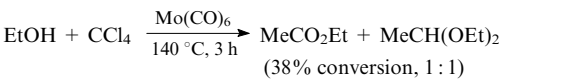
It is known that alkyl hypohalites (ROX) and hypochlorous (hypobromous) acid (HOX) are strong oxidants; therefore, the generation of these species *in situ* under the action of molybdenum complexes has been used in a series of studies to conduct oxidation reactions.[119, 122] In particular, it was found that ROX and HOX actively oxidize the initial alcohols and convert them to aldehydes (acetals), ketones (ketals) and esters.[119, 122] For example, methanol reacts with CCl_4 in the presence of $Mo(CO)_6$ to give dimethoxymethane (Scheme 56).[119]

Scheme 56



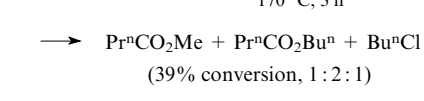
Under similar conditions, ethanol is converted to ethyl acetate and diethoxyethane (Scheme 57).[119]

Scheme 57



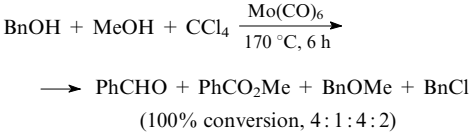
Higher primary alcohols, for example, butyl alcohol, react non-selectively with CCl_4 in the presence of $Mo(CO)_6$. In parallel to oxidation, substitution chlorination of alcohol at the OH group takes place. However, if methanol, which is readily oxidized to methyl hypochlorite, is added to the reaction mixture (ROH : MeOH = 1 : 1), the oxidation becomes the major pathway of transformation of higher alcohols (Scheme 58).[119]

Scheme 58



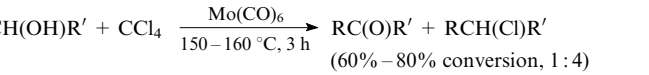
Under similar conditions, benzyl alcohol is oxidized to give benzaldehyde, methyl benzoate and benzyl methyl ether. Benzyl chloride is formed as a side product (Scheme 59).

Scheme 59



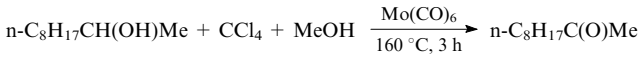
The oxidation of secondary alcohols under the action of CCl_4 in the presence of $Mo(CO)_6$ results in the formation of ketones. However, their yields are, most often, moderate, because the substitution chlorination is the predominant pathway of the reaction between CCl_4 and secondary alcohols (Scheme 60).[119]

Scheme 60



However, if the reaction is carried out with the addition of methanol, which is easily oxidized to methyl hypochlorite, the yield of the ketone considerably increases (Scheme 61).[119]

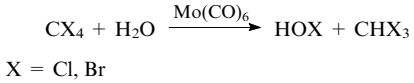
Scheme 61



(57% conversion, 90% selectivity)

It was found that $Mo(CO)_6$ catalyzes the reaction of halomethanes (CCl_4, CBr_4 and $CBrCl_3$) with one more compound containing a hydroxy group, namely, with water. In this case, the reaction products are hypochlorous or hypobromous acid and chloroform or bromoform (Scheme 62).[123–125]

Scheme 62



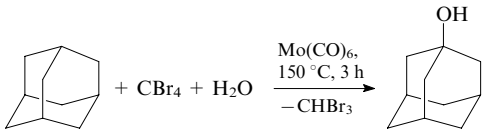
X = Cl, Br

The concentration of HOX depends on many factors (temperature, nature of the halogen, reaction time and the presence of other substrates) and can reach 3.2 mg ml^{-1} for HOCl and 8.5 mg ml^{-1} for HOBr.[123–125]

It is known that hypochlorous and hypobromous acids are stronger oxidants than alkyl hypohalites. For this reason, their *in situ* generation in the $H_2O-CX_4-Mo(CO)_6$ system was employed to carry out the oxidative transformations of hydrocarbons.

Using the $CBr_4-H_2O-Mo(CO)_6$ system, adamantane was oxidized to adamantan-1-ol.[123,126] Simultaneously, CBr_4 was converted to bromoform (Scheme 63).

Scheme 63

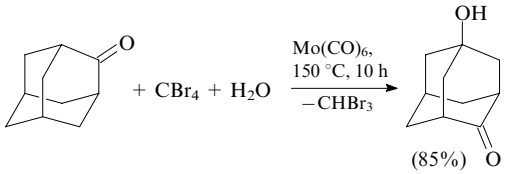


(85%)

According to iodometric titration, apart from adamantanol and $CHBr_3$, the reaction mixture contained 'active bromine' in a concentration of 0.9 mg ml^{-1}. The authors assumed that hypobromous acid, which is formed *in situ* during the reaction, is responsible for the oxidation.

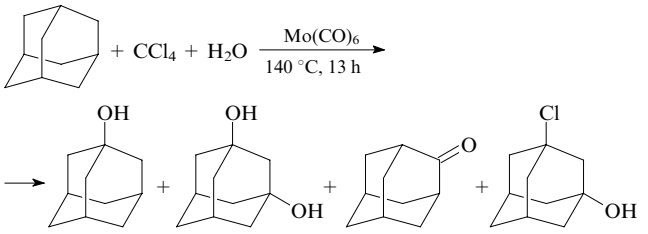
The oxidation of adamantan-2-one under similar conditions occurs over a period of 10 h and gives 1-hydroxyadamantan-4-one (Scheme 64).[127]

Scheme 64



The replacement of CBr_4 in the oxidative system by CCl_4 decreases the reaction temperature to 140 °C; however, more prolonged heating (13 h) is needed in this case to reach the complete adamantane conversion.[124] Owing to side reactions, in particular, chlorination, the composition of products is more complex: along with adamantan-1-ol, the reaction mixture was found to contain adamantane-1,3-diol, adamantan-2-one and 3-chloroadamantan-1-ol (Scheme 65).

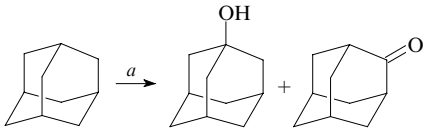
Scheme 65



(100% conversion, 4 : 2 : 1 : 1)

The selectivity of the reaction of adamantane with the $CCl_4-H_2O-Mo(CO)_6$ system considerably increases upon the addition of a phase transfer catalyst — tetra-n-butylammonium bromide (TBAB) ($[Mo(CO)_6] : [TBAB] = 1 : 1$). In this case, adamantan-2-one is formed as the major product (Scheme 66).[124] According to authors' assumption, the agent responsible for adamantane oxidation is hypochlorous acid, the presence of which in the reaction mixture was confirmed by the presence of an absorption peak at 229 – 236 nm typical of HOCl that was observed in the UV spectrum.[128]

Scheme 66

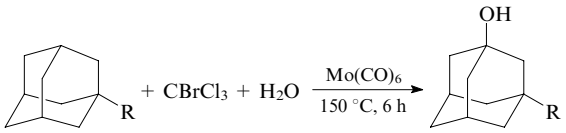


(100% conversion, 1 : 2)

(*a*) CCl_4, H_2O, $Mo(CO)_6$, TBAB (1 : 1), 140 °C, 13 h

1-Substituted adamantanes, including adamantan-1-ol, 1-chloro-, 1-bromo-, 1-acetyl-, 1-amino- and 1-(1-aminoethyl)adamantanes and adamantane-1-carboxylic acid undergo hydroxylation on treatment with the $CBrCl_3-H_2O-Mo(CO)_6$ oxidative system (Scheme 67).[124]

Scheme 67



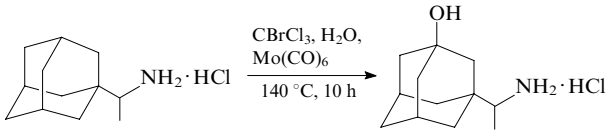
$[Mo(CO)]_6 : [substrate] : [CBrCl_3] : [H_2O] = 1 : 100 : 100 : 4000$

R	Product yield (%)	R	Product yield (%)
OH	86	NH_2	80
Cl	80	$CH(NH_2)Me$	98
Br	92	CO_2H	58
Ac	98		

1-(1-Aminoethyl)adamantane was hydroxylated with the $CBrCl_3-H_2O-Mo(CO)_6$ oxidative system.[129] The reaction proceeded at catalyst concentrations below 3 mol.% with a substrate conversion of 99% (Scheme 68).

A second representative of the adamantane series, diamantane (**101**), is oxidized rather actively (up to 75% conversion) with the $CBrCl_3-H_2O-Mo(CO)_6$ system furnishing a mixture of 1-hydroxy- (**102a**) and 4-hydroxy-

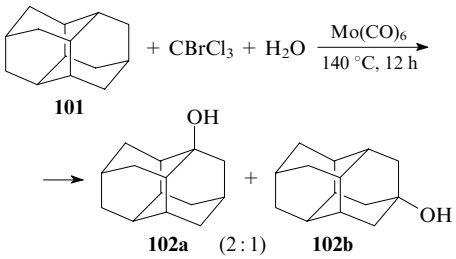
Scheme 68



$[Mo(CO)]_6 : [substrate] : [CBrCl_3] : [H_2O] = 3 : 100 : 100 : 4000$

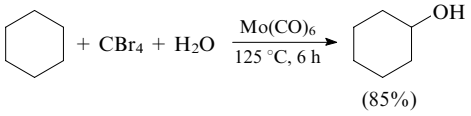
diamantanes (**102b**) (2 : 1) in a total yield of 75% (Scheme 69).[124]

Scheme 69



The $CBr_4 - H_2O - Mo(CO)_6$ system selectively oxidizes cyclohexane to give cyclohexanol (Scheme 70).[130]

Scheme 70



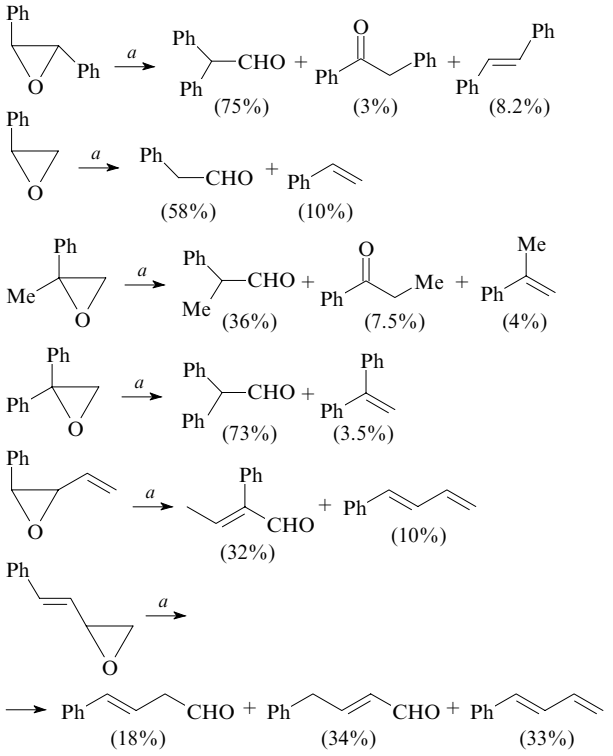
VII. Transformations of epoxides under the action of molybdenum complexes

Molybdenum complexes catalyze various reactions of epoxides. For example, molybdenum hexacarbonyl facilitates the isomerization of epoxides to give ketones and aldehydes.[131] Refluxing of dimethoxyethane solutions of 2-phenyloxirane, 2,3-diphenyloxirane, 2-methyl-2-phenyloxirane, 2,2-diphenyloxirane, 3-phenyl-2-vinyloxirane and 2-phenylvinyloxirane in the presence of catalytic amounts of $Mo(CO)_6$ gives rise to the corresponding aldehydes in 18% – 75% yields (Scheme 71). A side reaction is deoxygenation of the epoxide, resulting in the parent alkene. In the case of 2,3-diphenyl- and 2-methyl-2-phenyloxiranes, minor amounts of ketones are also formed.

The isomerization of α-pinene oxide, resulting in a mixture of products comprising **103** – **106** and other compounds, was accomplished using molybdenum indenyl complexes: $IndMo(\eta^3\text{-}C_3H_5)(CO)_2$ (**107a**), $(Me\text{-}Ind)Mo(\eta^3\text{-}C_3H_5)(CO)_2$ (**107b**) and $(Me_3\ Si\text{-}Ind)Mo(\eta^3\text{-}C_3H_5)(CO)_2$ (**107c**) (Me-Ind and Me_3Si-Ind are 1-methyl- and 1-trimethylsilylindenyl, respectively).[132] The activities of molybdenum complexes **107a** – **c** towards isomerization of pinene oxide are nearly equal, but are still lower than the activity of the tungsten indenyl complex $IndW(\eta^3\text{-}C_3H_5)(CO)_2$ (**108**) (Scheme 72).

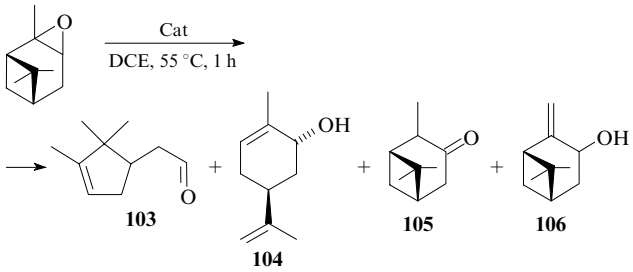
Whereas in the presence of a catalytic amount of $Mo(CO)_6$, epoxides are mainly converted to aldehydes, heating with a stoichiometric amount of $Mo(CO)_6$, results in deoxygenation to give the parent alkenes (Scheme 73).[133]

Scheme 71



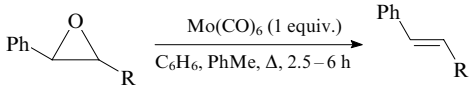
(*a*) $Mo(CO)_6$, $MeO(CH_2)_2OMe$, 85 °C

Scheme 72



Catalyst	Substrate conversion (%)	Selectivity (%)				
		103	**104**	**105**	**106**	other products
107a	64	52	19	7	5	17
107b	66	57	19	10	6	8
107c	61	54	19	6	4	17
108	93	57	20	5	8	10

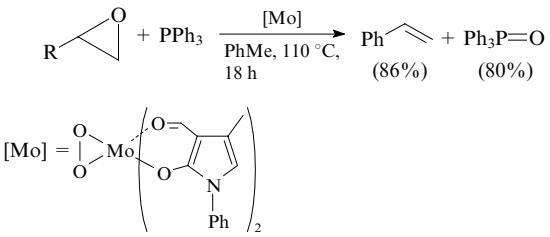
Scheme 73



R = Bz (70% yield), CO_2Et (90%), CH_2OAc (88%), Ph (84%)

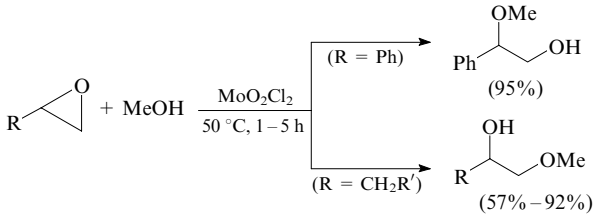
When triphenylphosphine is used as the oxygen acceptor in the deoxygenation of 2-phenyloxirane to give styrene, no excess catalyst is needed (Scheme 74).[134]

Scheme 74



Owing to its acidic properties, molybdenum(VI) dichloride dioxide serves as an efficient catalyst for the methanolysis of a wide range of epoxides (Scheme 75).[135]

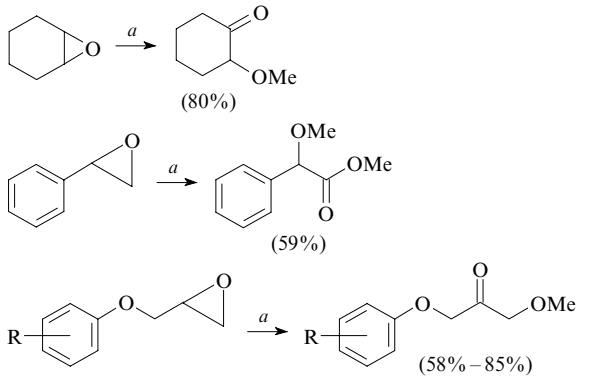
Scheme 75



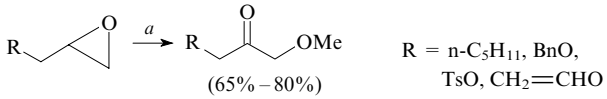
R = Ph, 3,4-$(MeO)_2C_6H_3CH_2$, $PhOCH_2$, 4-$HOC_6H_4OCH_2$, $BnOCH_2$, $TsOCH_2$, $AllOCH_2$, Hex, 4-$HOCH_2C_6H_4OCH_2$, *etc.*; Ts = 4-$MeC_6H_4SO_2$

If epoxides react with methanol in the presence of an oxidant, oxone, the reaction does not stop after methanolysis, but is accompanied by oxidation of the formed OH group to the oxo group (Scheme 76).[135]

Scheme 76



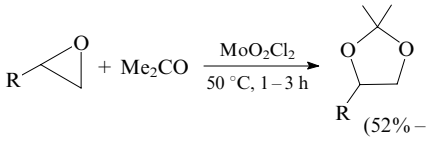
R = H, OH, CHO, $OSiBu^tMe_2$



(*a*) MeOH, $KHSO_5$, MoO_2Cl_2

On treatment with acetone in the presence of MoO_2Cl_2, epoxides are converted to acetonides (Scheme 77).[135]

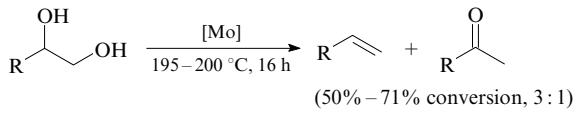
Scheme 77



R = Ph, 3,4-$(MeO)_2C_6H_3CH_2$, $PhOCH_2$, 4-$HOC_6H_4OCH_2$, $BnOCH_2$, $TsOCH_2$, $AllOCH_2$, Hex, 4-$HOCH_2C_6H_4OCH_2$, *etc.*

Molybdenum compounds were used to convert a number of 1,2-diols, usually prepared from epoxides, to alkenes. The process comprising deoxygenation and dehydration occurs under drastic reaction conditions (Scheme 78).[136, 137]

Scheme 78

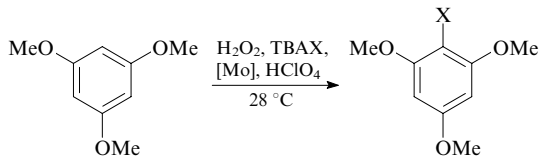


R = Bu^n, n-$C_{10}H_{21}$; [Mo] = MoO_2Me_2(bipy), $(NH_4)_6Mo_7O_{24}$, MoO_2Cl_2(bipy)

VIII. Molybdenum complexes in halogenation reactions

Molybdenum complex **90b** containing tris-*tert*-butylphenolamine in the coordination sphere and MoO_2Cl_2, which are stable in acidic aqueous solutions, catalyze the oxidative halogenation of aromatic compounds, in particular, 1,3,5-trimethoxybenzene, with tetra-n-butylammonium bromide or chloride (TBAB or TBAC) and hydrogen peroxide (Scheme 79).[102]

Scheme 79



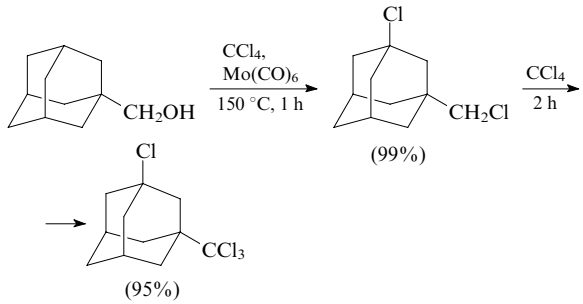
[Mo] : [substrate] : [TBAX] : $[H_2O_2]$: $[HClO_4]$ = 0.05 : 20 : 0.1 : 40 : 20

X	[Mo]	$t_{1/2}$ (H_2O_2)/min	Yield (%)
Br	**90b**	24	99
Br	MoO_2Cl_2	24	99
Cl	**90b**	–	20

It is noteworthy that vanadium compounds are more active catalysts for these reactions.[138]

Chlorination of adamantane and its derivatives with CCl_4, which serves as the source of chlorine, in the presence of molybdenum hexacarbonyl has been reported.[139] In the case of 1-hydroxymethyladamantane, not only chlorination of the adamantane cage takes place, but also the alcoholic OH group is replaced (Scheme 80).

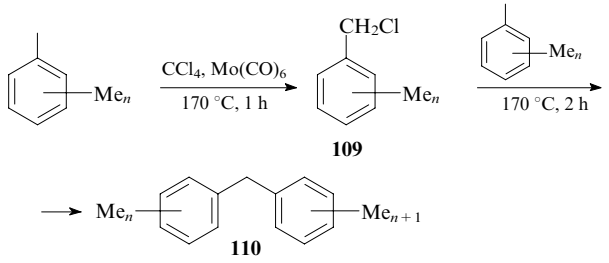
Scheme 80



A more active chlorination catalyst is formed upon the addition of acetonitrile to $Mo(CO)_6$. The $Mo(CO)_6$ – MeCN catalytic system can be used to chlorinate toluene and xylenes with CCl_4 to give benzyl chlorides **109**, which then perform Friedel – Crafts alkylation of the initial methylar-

enes to give diarylmethanes **110** [Scheme 81, for *m*-xylene ($n = 1$), the total yield of two isomers **110** is given].[140]

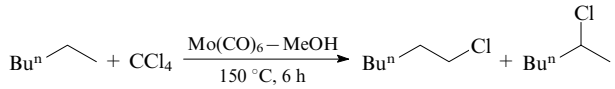
Scheme 81



n	Isomer	Yield of **109** (%)	Yield of **110** (%)
0		50	78
1	*ortho*	16	74
	meta	18	72
	para	70	90

Alkyl hypohalites, which are prone to decomposition to give RO$^{\bullet}$ and X$^{\bullet}$ free radicals, were generated *in situ* from CX_4 and alcohols under the action of Mo complexes [139, 140] to be used subsequently to initiate halogenation of alkanes and cycloalkanes with CCl_4. For example, it was found that $Mo(CO)_6$ catalyzes chlorination of hexane with CCl_4 in the presence of methanol ($CCl_4 : MeOH = 1 : 1$).[121] The reaction gives a mixture of 1- and 2-chlorohexanes (Scheme 82).

Scheme 82

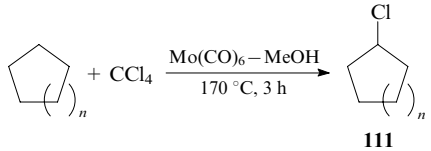


(81% conversion, 1 : 19)

According to iodometric titration data, the reaction mixture contains 'active chlorine'; its concentration after 20 min is 3.5 mg ml^{-1}. In the absence of methanol, the reaction does not proceed.

A similar reaction with the $CCl_4 - MeOH - Mo(CO)_6$ system can be carried out for cyclic hydrocarbons, cyclopentane and cyclohexane, which are selectively converted to monochlorinated derivatives **111**, the conversion being incomplete (Scheme 83).[121]

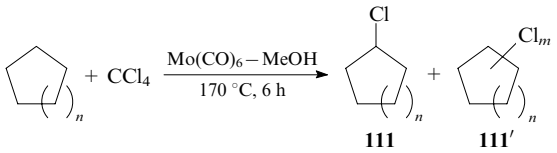
Scheme 83



$n = 1$ (70% yield), 2 (68%)

A twofold increase in the reaction time (170 °C, 6 h) results in complete conversion of the cycloalkanes, but in this case, the reaction gives a complex mixture of mono- (**111**), di- and trichloro derivatives (**111′**), the ratio of which depends on the ring size in the starting hydrocarbon (Scheme 84).

Scheme 84

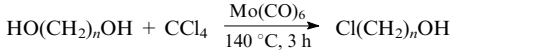


$m = 2, 3$

n	Conversion (%)	**111** : **111′** ratio	*n*	Conversion (%)	**111** : **111′** ratio
1	87	1.4 : 1	4	95	1.8 : 1
2	97	2 : 1	8	82	1 : 1.4

The reaction of CCl_4 with α,ω-diols in the presence of $Mo(CO)_6$ follows a peculiar pathway. Instead of the expected oxidation, substitution chlorination of one of the diol hydroxy groups takes place to furnish α,ω-chlorohydrins in high yields (Scheme 85).[119, 122]

Scheme 85



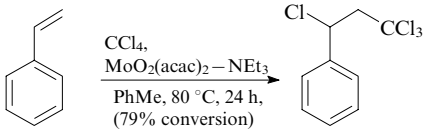
n = 3 (98% yield), 4 (98%), 5 (95%), 6 (98%), 7 (87%), 9 (74%), 12 (48%)

IX. Molybdenum complexes as catalysts of the Kharasch reaction

Molybdenum complexes are effective catalysts of the Kharasch reaction — the addition of halomethanes to alkenes.[141]

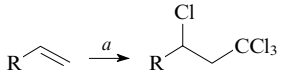
A distinctive feature of Mo catalysts compared with classic copper- and iron-based catalysts of telomerization is the regioselectivity of addition of the Cl$^{\bullet}$ and $^{\bullet}CCl_3$ radicals to a multiple bond. It is worth noting that molybdenum complexes show a significant activity in the Kharasch reaction when combined with nucleophilic co-initiators. For example, molybdenyl acetylacetonate [$MoO_2(acac)_2$] activated by triethylamine catalyzes the regioselective addition of CCl_4 to styrene to give 1,1,1,3-tetrachloro-3-phenyl-

Scheme 86

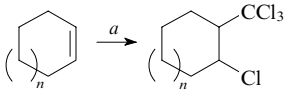


(67%)

[styrene] : [CCl_4] : [$MoO_2(acac)_2$] : [NEt_3] = 100 : 400 : 1 : 5



R = Bu^n (80% yield), n-C_5H_{11} (85%)

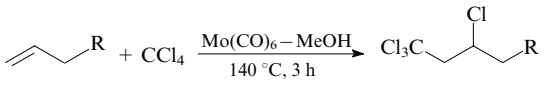


n = 1 (23% yield), 3 (88%);
(*a*) CCl_4, $Mo(CO)_6$, MeCN, 80 °C

propane in a 53% overall yield (Scheme 86).[142] Acetonitrile was proposed as a nucleophilic co-initiator to activate $Mo(CO)_6$ (see Scheme 86).[143]

Relatively active Mo catalysts for the addition of CCl_4 to alkenes are formed when alcohols are used as nucleophilic co-initiators (Scheme 87).[120] In the authors' opinion, the beneficial effect of alcohols is due to the *in situ* generation of alkyl hypochlorites, which are prone to decomposition with the formation of the $RO^{\bullet}$ and $Cl^{\bullet}$ radicals. According to iodometric titration, 'active chlorine' (1.3 – 2.1 mg ml^{-1}) is present in the reaction mixture containing CCl_4, methanol, $Mo(CO)_6$ and alkene; this is indicative of the formation of methyl hypochlorite, which is likely to initiate, together with $Mo(CO)_6$, the reaction of CCl_4 with alkenes.

Scheme 87

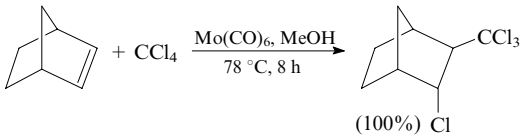


R = Pr^n (85% yield), n-C_5H_{11} (94%)

Despite the drastic conditions (140 °C), the addition of CCl_4 to linear alkenes is highly regioselective: the reaction gives unbranched isomers.[120]

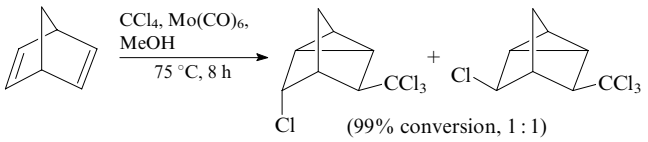
The addition of CCl_4 to norbornene in the presence of $Mo(CO)_6$ – MeOH proceeds very readily and selectively. As a result, one out of the four possible isomers — 2-*endo*-chloro-3-*exo*-trichloromethylbicyclo[2.2.1]heptane — is formed in a quantitative yield (Scheme 88).[120]

Scheme 88



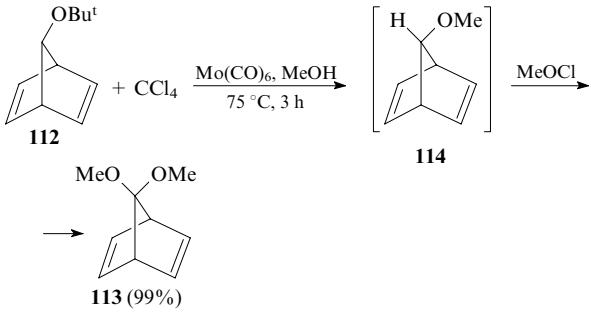
Norbornadiene reacts with the CCl_4 – MeOH – $Mo(CO)_6$ system in a similar way to give two isomeric products in equivalent amounts (Scheme 89).[120, 125]

Scheme 89



However, 7-*tert*-butoxynorbornadiene (**112**) reacts with the CCl_4 – MeOH – $Mo(CO)_6$ system in a different way: the reaction gives 7,7-dimethoxynorbornadiene (**113**) in a quantitative yield (Scheme 90).[120, 125, 144]

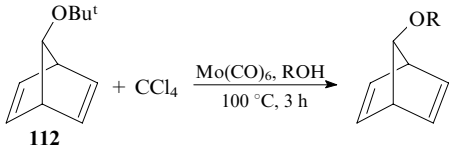
Scheme 90



It is evident that product **113** is formed stepwise: the first step is transesterification of substrate **112** with methanol, and the subsequent oxidation of 7-methoxynorbornadiene (**114**) with methyl hypochlorite gives rise to the final dimethoxynorbornadiene. The structure of product **113** is indicative of the *in situ* formation of methyl hypochlorite. The presence of MeOCl in the reaction mixture is additionally confirmed by the data of iodometric titration: the concentration of 'active chlorine' is 1.3 – 2.0 mg ml^{-1}.

This transformation is specific and proceeds only with the participation of methanol. The attempts to extend it to other alcohols — ethanol and propan-1-ol — were unsuccessful: the reactions of 7-*tert*-butoxynorbornadiene (**112**) with these alcohols stopped after the transesterification step (Scheme 91).[116, 141, 142]

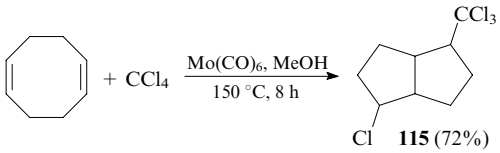
Scheme 91



R = Et (96% yield), Pr^n (68%)

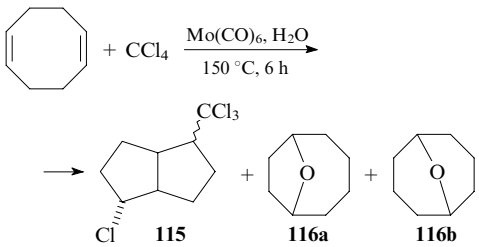
Cycloocta-1,5-diene reacts with CCl_4 under the action of $Mo(CO)_6$ – MeOH. The reaction requires drastic conditions (150 °C, 8 h) and is complicated by the transannular rearrangement characteristic of this substrate (Scheme 92).

Scheme 92



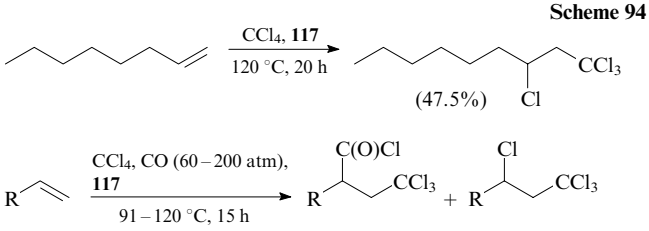
When the reaction is carried out in the presence of water, the yield of product **115** decreases to 37% and the selectivity decreases as a result of formation of 1,4- (**116a**) and 1,5-epoxycyclooctanes (**116b**) (Scheme 93).[128]

Scheme 93



A special case of molybdenum catalysts for the addition of CCl_4 to alkenes is the binuclear complex $Mo_2(CO)_6(\eta^5\text{-}Cp)_2$ (**117**), which exhibits activity without nucleophilic co-initiators.[145 – 147] Drawbacks of this catalyst include the difficulty of preparation as well as drastic reaction conditions and a long reaction time (Scheme 94). In the reactions of alkenes with CCl_4 and CO, the product ratio is determined by the nature of the substrate; in the case of ethylene (R = H), only acid chloride is formed (see Scheme 94).

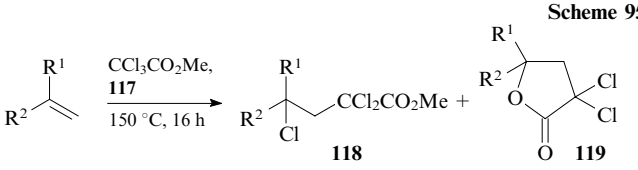
Scheme 94



R	Acid chloride : tetrachloride (by mass)
Me	0.59
Et	1.71
Bu^n	1.52

The same molybdenum complex **117** catalyzes the reaction of alkenes with methyl trichloroacetate, resulting in a mixture of acyclic ester **118** and lactone **119**, with the latter predominating (Scheme 95).[147]

Scheme 95



R^1	R^2	Yield (%)		R^1	R^2	Yield (%)	
		118	**119**			**118**	**119**
Bu^n	H	6.8	68.3	n-C_5H_{11}	H	10.2	73.8
Et	H	4.4	50.8	Me	Me	13.6	42.1

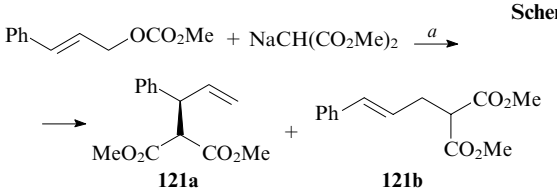
X. Allylic alkylation of C-nucleophiles

Like Ni, W, Pd, Rh, Ru and Ir compounds, molybdenum complexes are efficient catalysts of allylic alkylation of C-nucleophiles.[15, 148] This reaction, which is known in the literature by the names of discoverers, Tsuji and Trost, has aroused considerable interest of researchers since the 1970s, because the formation of a new C – C bond is accompanied by the appearance of a chiral centre, which creates prerequisites for asymmetric induction. The allylic alkylation, including the asymmetric allylic alkylation (AAA), induced by molybdenum complexes has been studied in detail in relation to the reactions of allyl acetates, allyl carbonates and allyl phosphates with sodium dimethyl malonate.[16, 149 – 157]

Molybdenum catalysts for allylic alkylation have a number of distinctive features: they are tolerant to most functional groups in the reactants; furthermore, they facilitate the selective formation of branched isomers, which is of prime importance for the targeted synthesis of chiral compounds.[149 – 151] The focused studies of Trost and coworkers demonstrated that the addition of chiral ligand (*R*,*R*)-**120a** to a Mo-containing catalyst makes it possible to perform allylic alkylation to give, for example, products **121a**,**b**, **122** and **123a**,**b** with enantioselectivity of up to 99% (Scheme 96).[152 – 154]

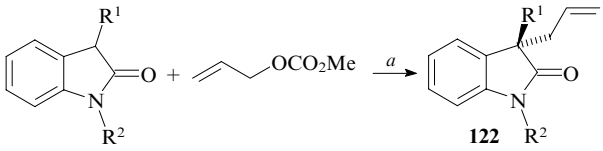
The most brilliant achievements of the asymmetric allylic alkylation are also associated with the works of Trost, who introduced a large library of chiral ligands, (*S*,*S*)- and (*R*,*R*)-diaminocyclohexane derivatives, into the

Scheme 96



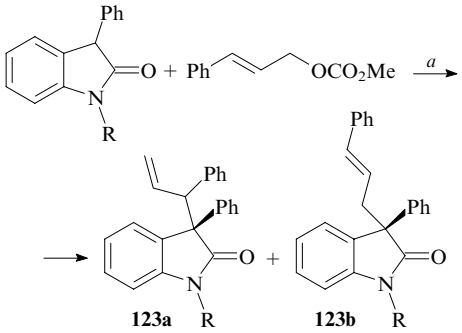
(**121a** : **121b** = 49 : 1, for **121a**, *ee* is 99%)

(*a*) $(EtCN)_3Mo(CO)_3$ – (*R*,*R*)-**120a** (1 : 1.5), THF, rt, 3 h



(*a*) Mo(η^3-C_7H_8)$(CO)_3$ – (*R*,*R*)-**120a** (1 : 1.5), LiOBu^t, THF, rt

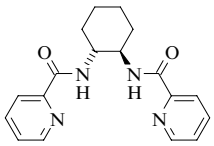
R^1	R^2	Yield of **122** (%)	*ee* (%)
Me	Me	99	81
Me	Bn	93	75
Pr^i	Me	96	91
Pr^i	Bn	98	85



(*a*) Mo(η^3-C_7H_8)$(CO)_3$ – (*R*,*R*)-**120a** (1 : 1.5), NaOBu^t, THF, 60 °C

R	Yield of **123a** + **123b** (%)	**123a** : **123b** ratio	*ee* (%)
Boc	91	5 : 1	93
$MeOCH_2$	90	19 : 1	92
Bn	85	17 : 1	90
Me	88	18 : 1	92

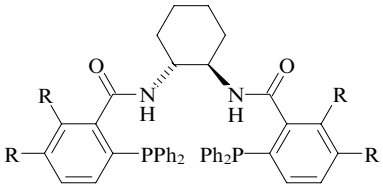
C_7H_8 is cycloheptatriene; (*R*,*R*)-**120a** = Boc = C(O)OBu^t



synthetic practice. Ligands (*R*,*R*)- and (*S*,*S*)-**120**, (*R*,*R*)- and (*S*,*S*)-**124** and (*R*,*R*)- and (*S*,*S*)-**125** are commercially available compounds. The interest in these ligands is reasonable, because they provide a nearly 100% enantioselectivity of the allylic alkylation.

The Trost catalysts are unstable in air, but they are prepared from $Mo(CO)_6$, which is stable under ambient conditions. Therefore, in some papers, $Mo(CO)_6$ activated by microwave (MW) radiation [155] is taken as the alkylation catalyst, while chiral ligands, 1,2-bis(pyridine-2-carboxamido)cyclohexane derivatives (*R*,*R*)-**120a** – **g**, are added; in this case, the product yield and the reaction enantioselectivity can be increased to almost 100% (Scheme 97).[16, 156]

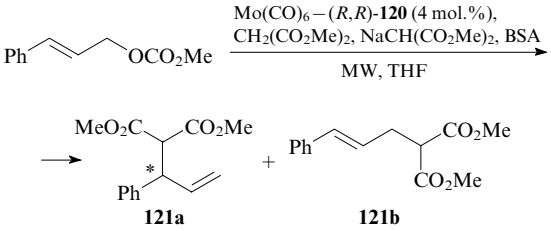
Structures 124, 125



(*R*,*R*)-**124**, (*R*,*R*)-**125**

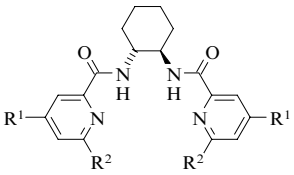
R = H (**124**),
R – R is benzo (**125**)

Scheme 97



(*R*,*R*)-**120**	*T*/°C	*t* /min	Yield of **121a** + **121b** (%)	**121a** : **121b** ratio	*ee* (%)
a	160	6	80	19 : 1	98
b	150	15	37	16 : 1	97
c	165	5	46	13 : 1	98
d	165	4	88	41 : 1	> 99
e	165	6	89	74 : 1	96
f	170	12	91	88 : 1	96
g	165	5	30	13 : 1	79

(*R*,*R*)-**120a** – **g** =



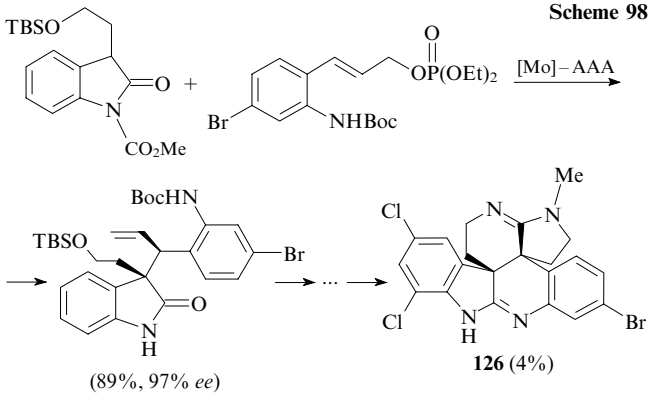
BSA is bis(trimethylsilyl)acetamide

Compound **120**	R^1	R^2	Compound **120**	R^1	R^2
a	H	H	**e**	Cl	H
b	NO_2	H	**f**	pyrrolidino	H
c	Bu^t	H	**g**	H	Me
d	OMe	H			

There are numerous known examples of the successful use of Mo-catalyzed allylic alkylation for the synthesis of chiral compounds, which are described in a number of papers, reviews and monographs.[15, 16, 148, 155 – 157] A remarkable example of such reactions was reported by Trost *et al.*,[158] who performed the total synthesis of the natural polycyclic alkaloid, (–)-perophoramidine (**126**), which has a marked anticancer activity (Scheme 98).

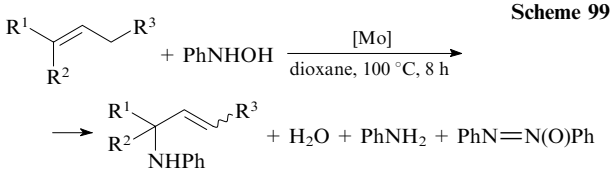
In addition to allylic alkylation, molybdenum complexes catalyze the allylic amination. Srivastava *et al.*[159, 160] accomplished allylic amination of phenylhydroxylamine under the action of molybdenum dioxo complexes and obtained products **127** in moderate or low yields (Scheme 99).

Scheme 98



[Mo] = $(C_7H_8)Mo(CO)_3$ – (*S*,*S*)-**120a**, TBS = $SiBu^tMe_2$

Scheme 99



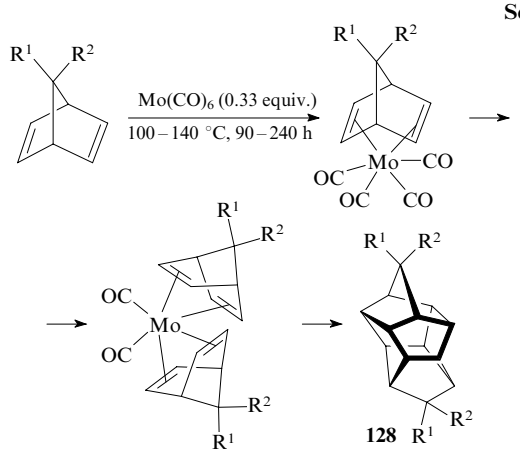
[Mo] = MoO_2(dipic)(HMPA), $MoO_2(dtc)_2$ (dipic is pyridine-2,6-dicarboxylate)

R^1	R^2	R^3	Yield of **127** (%)
Me	Me	Pr^n	52
Me	Me	H	42
H	H	Bn	11
H	$(CH_2)_4$		4

XI. Oligomerization reactions

Molybdenum hexacarbonyl catalyzes dimerization of norbornadiene and its derivatives according to the [4π + 4π] pattern to give heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecanes **128**. Despite the low yields, which depend on the reaction conditions and time, the reaction is distinguished by high selectivity to dimers **128** (Scheme 100).[161 – 164]

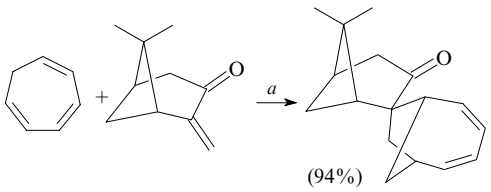
Scheme 100



R^1 = H: R^2 = H (29% – 40% yields), OBz (3%), OBu^t (14%);
R^1 – R^2 = $(CH_2)_4$ (13%)

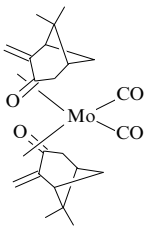
Molybdenum complex **129** with (1*R*)-(+)-pinocarvone coordinated to the metal in the η^4-fashion induces [6+2]-cycloaddition of cycloheptatriene to (1*R*)-(+)-pinocarvone (Scheme 101).[165]

Scheme 101



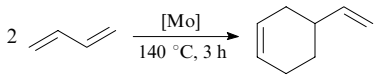
(*a*) **129** (5 mol.%), THF, 50 °C: Ar, 12 h or in air, 1 h

129 =



Molybdenum complexes are efficient catalysts for cyclodimerization of buta-1,4-diene to give 4-vinylcyclohex-1-ene; the reaction is carried out in a CCl_4 – MeOH mixture (Scheme 102).[166]

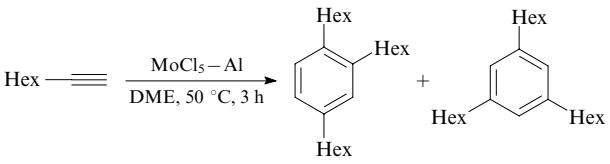
Scheme 102



[Mo] = $Mo(CO)_6$ (95% yield), $MoO_2(acac)_2$ (99%)

Molybdenum pentachloride reduced by main group metals (Al, Sn, In, Mg, Li) catalyzes cyclotrimerization of alkynes in dimethoxyethane (DME).[167] According to authors' assumption, Mg, Li Al, Sn and In are converted under reaction conditions to the metal halides, which are Lewis acids and catalyze alkyne cyclotrimerization together with the reduced Mo form. The product yields depend on the acidity of metal chlorides and decrease in the following sequence: $AlCl_3 > SnCl_4 > MgCl_2 > LiCl$. The highest yield of oct-1-yne cyclotrimers (1,2,4- and 1,3,5-tri-n-hexylbenzenes) was obtained with the $MoCl_5$ – Al system (Scheme 103).

Scheme 103

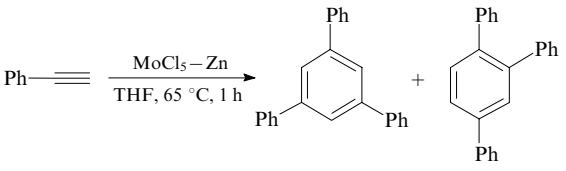


(90% conversion, 8 : 1)

[alkyne] : [$MoCl_5$] : [Al] = 3 : 1 : 1

A relatively active catalyst for acetylene cyclotrimerization is formed if metallic zinc is used to reduce $MoCl_5$ (Scheme 104).[168]

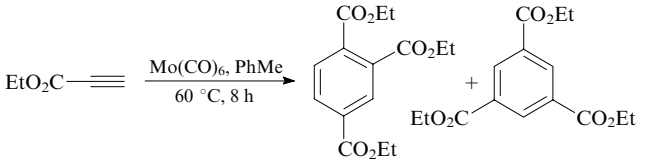
Scheme 104



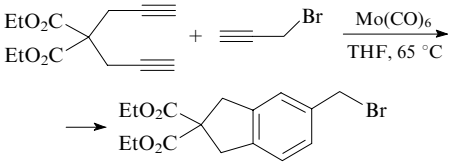
(80% conversion, 0.6 : 1.0)

Molybdenum hexacarbonyl catalyzes the cyclotrimerization of acetylenes in the absence of a reducing agent (Scheme 105).[169, 170]

Scheme 105



(100% conversion, 3 : 1)

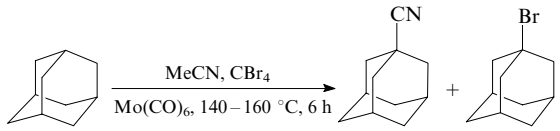


(65%)

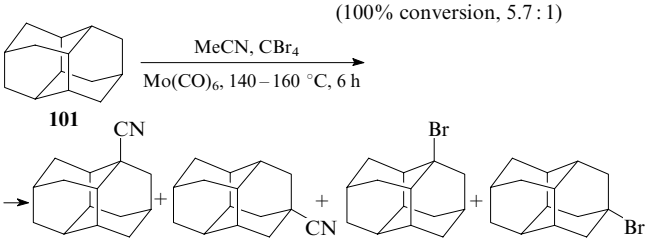
XII. Catalysis of C – C bond formation

The discovered possibility of direct $Mo(CO)_6$-catalyzed cyanation of adamantane and diamantane (**101**) with acetonitrile is of high synthetic potential. [171, 172] The reaction requires the presence of tetrabromomethane and proceeds at 140 – 160 °C for 6 h. In the case of adamantane, the yield of 1-cyanoadamantane is 85%. 1-Bromoadamantane is formed as a side product. Diamantane (**101**), the second representative of the diamondoid homologous series, undergoes a similar reaction with acetonitrile to be converted to a mixture of four products: 1- and 4- cyanodiamantanes, 1- and 4-bromodiamantanes (Scheme 106).

Scheme 106



(100% conversion, 5.7 : 1)

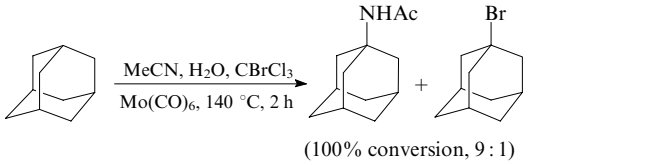


(68% conversion, 7.5 : 5 : 1.5 : 1)

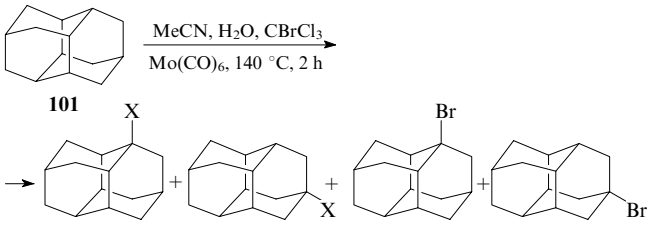
When the reaction is carried out in water and tetrabromomethane is replaced by $CBrCl_3$, the route of adamantane and diamantane reactions with acetonitrile changes towards amidation.[173, 174] As side products, the reactions give brominated adamantane and diamantane derivatives (Scheme 107).

The catalytic cyanation of the C – H bond can be accomplished with trimethylsilyl cyanide (Me_3SiCN), which reacts with *N*-aryltetrahydroisoquinolines in the presence of oxygen to give 1-cyanotetrahydroisoquinolines (α-aminonitriles) in high yield. This reaction is efficiently catalyzed by $MoO_2(acac)_2$ (Scheme 108).[175]

Scheme 107



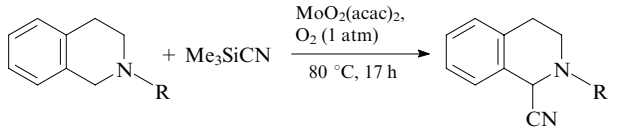
(100% conversion, 9 : 1)



(100% conversion, 2 : 1 : 0.5 : 0.4)

X = NHAc

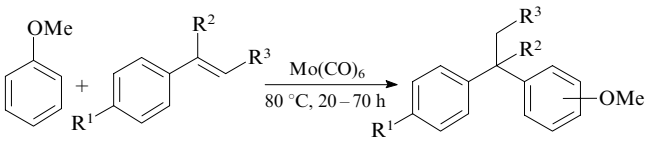
Scheme 108



[substrate] : [Me_3SiCN] : [$MoO_2(acac)_2$] = 0.5 : 1 : 0.05;
R = Ph (80% yield), 4-$MeOC_6H_4$ (82%)

The hexacarbonyl $Mo(CO)_6$ successfully catalyzes the Friedel – Crafts reaction, in particular, alkylation of anisole with styrene and its derivatives (Scheme 109).[176]

Scheme 109



R^1	R^2	R^3	Yield (%)	Selectivity (*ortho* : *meta* : *para*)
H	H	H	96	1 : 0 : 4
H	Me	H	79	1 : 0 : 12
H	H	Me	79	1 : 0 : 4
OMe	H	Me	97	1 : 0 : 19
Me	H	H	92	1 : 0 : 9

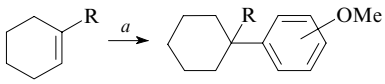
Reactions of the same type proceed with cyclohexene derivatives, some alcohols and 2-phenyloxirane (Scheme 110).

The best catalyst for the Friedel – Crafts acylation of aromatic compounds with benzoyl chloride is MoO_2Cl_2 (Scheme 111, the reaction gives the *para*-isomer or a mixture of *para*- and *ortho*-isomers in which the former predominates).[177]

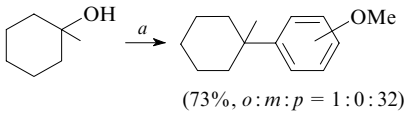
The reactions are carried out without a solvent or in bromobenzene under reflux. Attention is attracted by the relatively low consumption of MoO_2Cl_2 (20 mol.%), whereas the classic Lewis acids ($AlCl_3$ and $FeCl_3$) are usually taken in stoichiometric amounts.

Molybdenum hexacarbonyl catalyzes an unusual reaction of thiophene derivatives **130a – c** with carbon tetrachloride and alcohols, resulting in the formation of alkyl thiophene-2-carboxylates **131 – 133** (Scheme 112).[178]

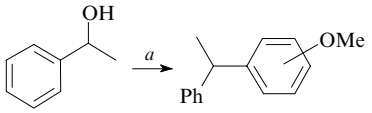
Scheme 110



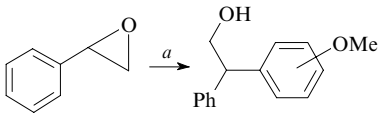
For R = H: 120 °C, 40 h (28% yield; *o* : *m* : *p* = 1 : 0 : 1);
for R = Me: 80 °C, 20 h (94% yield; *o* : *m* : *p* = 1 : 0 : 27)



(73%, *o* : *m* : *p* = 1 : 0 : 32)



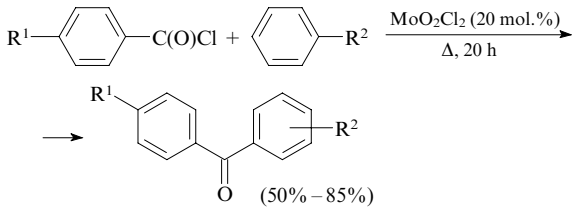
(91%, *o* : *m* : *p* = 1 : 0 : 4)



(21%, *o* : *m* : *p* = 1 : 0 : 4)

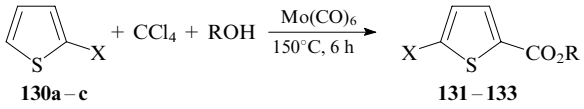
(*a*) MeOPh, $Mo(CO)_6$

Scheme 111



R^1 = Me, Cl, OMe, NO_2; R^2 = Me, OMe, SMe

Scheme 112



130a – c **131 – 133**

X = Cl (**130a**, **131**), Br (**130b**, **132**), I (**130c**, **133**)

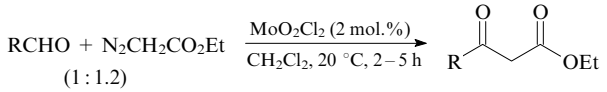
R	Yield (%)			R	Yield (%)		
	131	**132**	**133**		**131**	**132**	**133**
Me	65	77	24	Pr^n	–	63	–
Et	30	55	–	Pr^i	50	52	–

According to authors' assumption,[178, 179] this sophisticated reaction starts with the catalytic alkylation of thiophenes **130a – c** with carbon tetrachloride and ends with the subsequent alcoholysis of 2-trichloromethyl-substituted thiophenes. In the case of 2-bromo- and 2-iodothiophenes (**130b**,**c**), 5-chlorothiophene-2-carboxylates are also formed as a result of exchange reaction involving CCl_4.

The dichloride dioxide MoO_2Cl_2 catalyzes the reaction of ethyl diazoacetate with aldehydes. The reaction proceeds *via* the insertion of ethoxycarbonylcarbene into the C – H

bond of the aldehyde and results in esters of β-ketoacids (Scheme 113).[180]

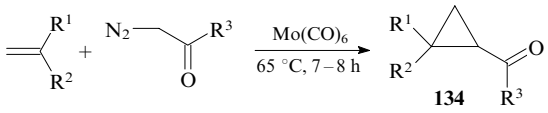
Scheme 113



R = Ph (90% yield), 2-Naph (73%), 4-MeC_6H_4 (85%), 4-$MeOC_6H_4$ (83%), 3,4,5-$(MeO)_3C_6H_2$ (88%), 4-$O_2NC_6H_4$ (92%), 4-BrC_6H_4 (82%), 2-Py (84%), 2-Fu (87%), Bn (95%), Am (95%); Fu is furyl

Molybdenum complexes catalyze one more reaction of diazo compounds, namely, the reaction of ethyl diazoacetate or α-diazoacetophenone with acrylic monomers (ethyl acrylate, acrylonitrile and methacrylonitrtile), which proceeds as cycloaddition to give products **134** (Scheme 114).[181]

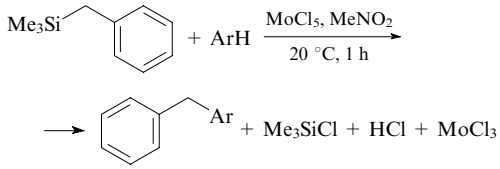
Scheme 114



R^1	R^2	Yield of **134** (%)	
		R^3 = Ph	R^3 = OEt
H	CO_2Et	72	31
H	CN	77	46
Me	CN	25	79

Molybdenum pentachloride in nitromethane catalyzes the cross-coupling of aromatic compounds with benzyltrimethylsilane, functioning simultaneously as an oxidant and a source of chlorine (Scheme 115).[182]

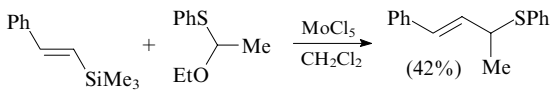
Scheme 115



ArH = PhH, PhMe, 1,3-$Me_2C_6H_4$, PhCl, PhF

An original method for C–C bond formation was reported by Hirao *et al.*[183] Trimethylstyrylsilane reacts with 1-ethoxyethyl phenyl sulfide in the presence of $MoCl_5$ to give the corresponding (*E*)-allyl sulfide (Scheme 116).

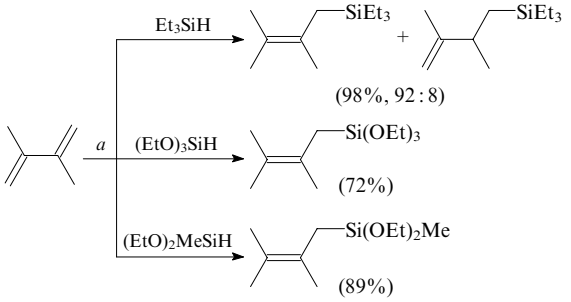
Scheme 116



XIII. Molybdenum complexes in hydrosilylation, hydrostannylation and hydrogermylation

Molybdenum complexes are active catalysts for hydrosilylation of unsaturated compounds with silanes. Molybdenum hexacarbonyl catalyzes the hydrosilylation of 2,3-dimethylbuta-1,3-diene with Et_3SiH, $(EtO)_3SiH$ or $(EtO)_2MeSiH$. The activity of $Mo(CO)_6$, unlike those of chromium and tungsten hexacarbonyls, remains unchanged upon the addition of Bu^tOOH, which acts as a co-initiator promoting the formation of radicals (Scheme 117).[184]

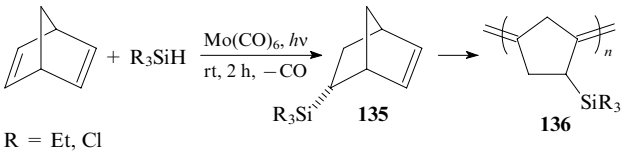
Scheme 117



(*a*) $Mo(CO)_6 - Bu^tOOH$, 100 °C, 24 h

The hydrosilylation of norbornadiene in the presence of $Mo(CO)_6$ under UV radiation can involve either one or both double bonds. 5-Triethyl- or 5-trichlorosilylnorbornene **135**, resulting from the monoaddition of R_3SiH to the substrate, undergoes ring opening metathesis polymerization under the reaction conditions to give product **136** (Scheme 118).[185] When diethylsilane is used, the monosilylated derivative is not identified, but a considerable amount of a disubstituted product is detected apart from the polymer.

Scheme 118



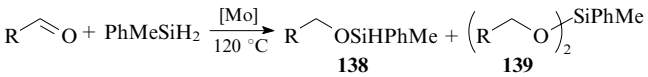
R = Et, Cl

Molybdenum complexes containing a bis-phosphine ligand **137** are efficient in hydrosilylation of aldehydes and ketones, but have low activity towards alkene hydrogenation (Scheme 119).[186] Indeed, aldehydes react with methylphenylsilane to give tri- (**138**) and tetrasubstituted silanes (**139**).

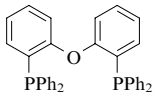
The dichloride dioxide MoO_2Cl_2 and the molybdenum complex $(ArN)Mo(H)(SiH_2Ph)(PMe_3)_3$ (**140**; Ar = 2,6-$Pr^i_2C_6H_3$)[187 – 190] showed a high catalytic activity towards the hydrosilylation of aldehydes and ketones at the C=O group (Scheme 120). The reaction involving complex **140** and phenylsilane afforded a mixture of di- (**141**) and trisubstituted silanes (**142**).

Molybdenum complexes are relatively efficient catalysts for alkyne hydrostannylation with organotin hydrides. Kazmaier and co-workers[191 – 194] investigated the hydrostannylation of various functionally substituted terminal alkynes with Bu^n_3SnH in the presence of $Mo(CO)_3(CNBu^t)_3$. Hydrostannylation was found to mainly follow Markovnikov's rule, which is indicative of an ionic mechanism of the reaction. Hydroquinone (HQ) was added to prevent radical hydrostannylation (Scheme 121).

Scheme 119

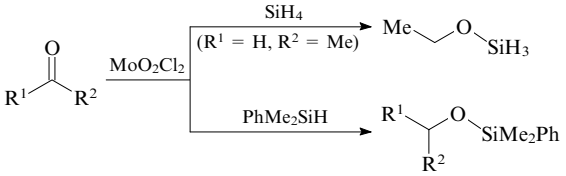


[Mo] = [Mo(NCMe)$_3$(NO)(**137**)][BAr$^F_4$];

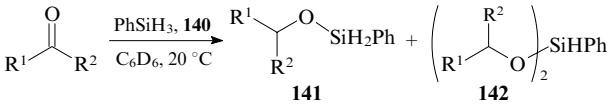
137 =  , Ar$^F_4$ = 3,5-(F$_3$C)$_2$C$_6$H$_3$

R	Time /h	Aldehyde conversion (%)	**138** : **139** ratio
4-MeOC$_6$H$_4$	2.5	29	29 : 0
4-MeC$_6$H$_4$	3	89	65 : 14
4-ClC$_6$H$_4$	2.5	100	82 : 18
4-FC$_6$H$_4$	< 3	100	57 : 43
4-NCC$_6$H$_4$	2.5	54	54 : 0
Cy	3	88	64 : 17
2-ClC$_6$H$_4$	0.25	61	61 : 0
Cyclohexen-4-yl	7	90	64 : 26
2-Fu	< 2	100	53 : 47
2-Thienyl	3	92	67 : 25
PhCH=CH	7	100	100 : 0

Scheme 120

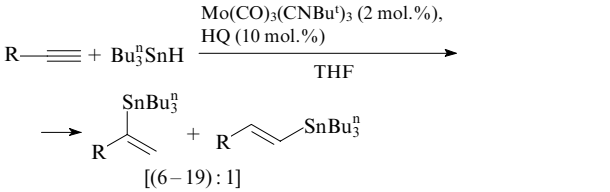


R^1 = H: R^2 = 4-F$_3$CC$_6$H$_4$ (100% yield), 4-MeO$_2$CC$_6$H$_4$ (100%);
R^1 = Me: R^2 = Ph(CH$_2$)$_2$ (76%)

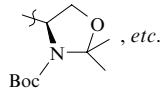


R^1	R^2	Time /h	Yield (%)	
			141	**142**
Ph	H	0.25	47	53
Me	Me	3.4	73	17

Scheme 121



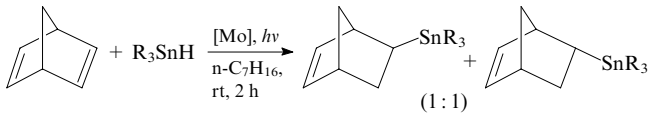
R = CH$_2$OH, CH$_2$OTHP, CH(Me)OTBDPS,

 , *etc.*

THP is tetrahydropyran-2-yl,
TBDPS = SiBu^{t}Ph$_2$

Norbornadiene was hydrostannylated in the presence of Mo(CO)$_6$ and Mo(CO)$_4$(η^4-nbd) (**143**, nbd is norbornadiene) under UV irradiation.[195] The reaction was carried out in an NMR tube (Scheme 122).

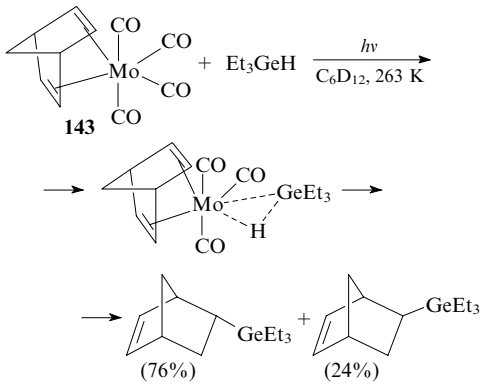
Scheme 122



[Mo] = Mo(CO)$_6$, Mo(CO)$_4$(η^4-nbd); R = Bu^n, Ph

Molybdenum carbonyls catalyze the hydrogermylation of norbornadiene with triethylgermane. The reaction was carried out for stoichiometric amounts of Mo(CO)$_4$(η^4-nbd) (**143**) and Et$_3$GeH under UV irradiation (Scheme 123).[196]

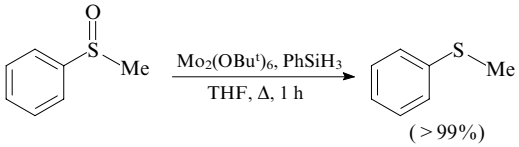
Scheme 123



XIV. Molybdenum complexes as catalysts of reduction reactions

Molybdenum alcoholates catalyze the reduction of sulfoxides with silanes to give the corresponding sulfides. The reduction of methyl phenyl sulfoxide in the presence of Mo$_2$(OBu^t)$_6$ was conducted to study the effect of the nature of silanes and solvents on the reaction route. The best results were obtained with phenylsilane in THF (Scheme 124).[66]

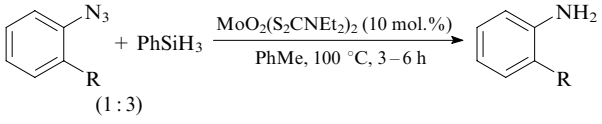
Scheme 124



[substrate] : [Mo$_2$(OBu^t)$_6$] : [PhSiH$_3$] = 100 : 1 : 100

Treatment of azides with phenylsilane in toluene in the presence of MoO$_2$(S$_2$CNEt$_2$)$_2$ leads to their reduction to give amines.[197] The reaction is chemoselective and can be

Scheme 125

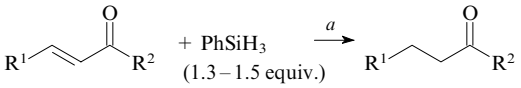


R = CHO (70% yield), OPr^n (65%), OBn (94%),
CH=CHCO$_2$Me (91%)

carried out for a broad range of functionally substituted azides (Scheme 125).

Molybdenum hexacarbonyl serves as an efficient catalyst for hydrogenation of α,β-unsaturated carbonyl compounds at the double bond on treatment with phenylsilane.[198] High selectivity of this reaction is noteworthy: the hydrogen atom adds exclusively to the C=C bond, while functional groups remain intact and have an insignificant effect on the reaction route, as the yields of hydrogenation products reach 100% (Scheme 126).

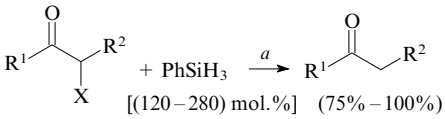
Scheme 126



R^1 = Ph, R^2 = Me; R^1 = H, R^2 = NPr^n_2, *etc.*;
(*a*) $Mo(CO)_6$ (3 mol.% – 5 mol.%), THF, Δ, 1.5 – 12 h

Molybdenum hexacarbonyl catalyzes the reductive dehalogenation of α-haloketones and α-halo-substituted esters on treatment with $PhSiH_3$ (Scheme 127).[199]

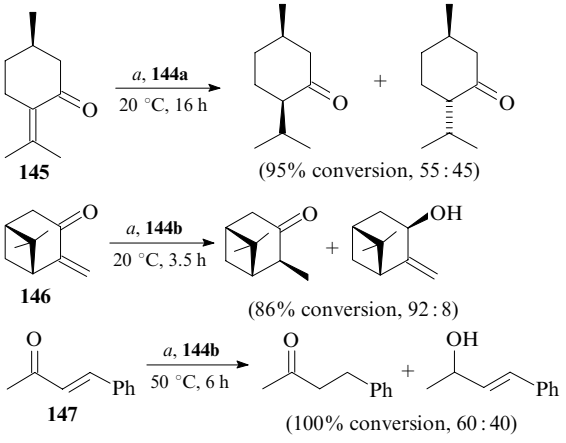
Scheme 127



X = Cl, R^2 = H: R^1 = Ph, OBu^n; X = Br, R^2 = Et: R^1 = Pr^n, OEt;
X = Br, R^2 = H: R^1 = Pr^i, Ph, 4-BrC_6H_4;
(*a*) $Mo(CO)_6 - PPh_3$ (1 : 3) (4 mol.% – 11 mol.%),
$NaHCO_3$ (80 mol.% – 250 mol.%), THF, Δ, 1.5 – 12 h

Dicarbonyl-bis(oxadiene)molybdenum complexes $Mo(CO)_2$(O-diene)$_2$ (**144a**,**b**) catalyze the reduction of α,β-unsaturated ketones **145** – **147** with phenylsilane.[200] The reaction is stepwise and proceeds *via* hydrosilylation and subsequent hydrolysis of the resulting compounds under the action of HF (Scheme 128).

Scheme 128

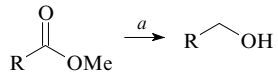


(*a*) 1) $PhSiH_3$, [Mo] (1 mol.%); 2) HF (aq., 5%);
[Mo] = $Mo(CO)_2$(O-diene)$_2$ [O-diene = **145** (**144a**), **146** (**144b**)]

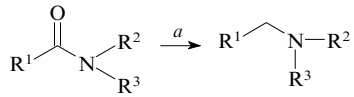
Mono- and dihydrosilanes have also been tested in these reactions; however, phenylsilane proved to be the best hydrogen donor. The reduction of α-haloketones with the $Mo(CO)_6 - PPh_3 - PhSiH_3$ system provides higher yields than the $Pd^0 - PhSiH_3$ system.

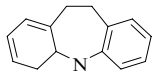
When trihydrosilanes, in particular, $PhSiH_3$, are used as hydrogen sources in the presence of MoO_2Cl_2, the reduction of carbonyl compounds takes place (Scheme 129).[201, 202]

Scheme 129

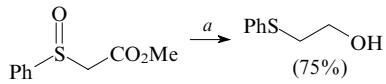


R = 4-$F_3CC_6H_4$ (79% yield), 4-ClC_6H_4 (75%), 4-BrC_6H_4 (72%),
Bn (81%), n-C_7H_{15} (81%), Pr^n (80%)



R^1 = Me: NR^2R^3 =  (87% yield),  (81%);

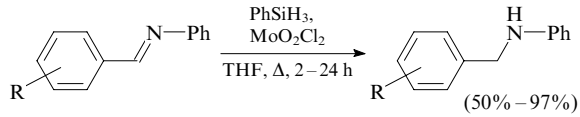
R^1 = Me, R^2 = H: R^3 = 4-BrC_6H_4 (56%), 4-ClC_6H_4 (52%);
R^1 = Ph, R^2 = H: R^3 = Ph (78%), Bn (40%);
R^1 = R^2 = 4-ClC_6H_4, R^3 = H (54%)



(*a*) $PhSiH_3$, MoO_2Cl_2, PhMe, Δ, 20 h

Phenylsilane also hydrogenates rather selectively the imino group in the presence of MoO_2Cl_2 (Scheme 130).[203]

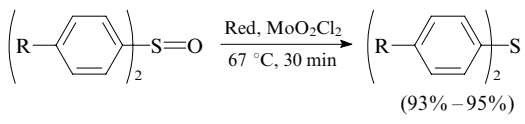
Scheme 130

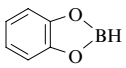


R = H, NO_2, CF_3, Cl, CO_2Me

Molybdenum dichloride dioxide catalyzes the reduction of sulfoxides with the BH_3 complex with THF or with catecholborane.[204] The reaction proceeds at room temperature over a period of 16 h, while a similar transformation in THF (67 °C) is completed in 15 – 20 min (Scheme 131).

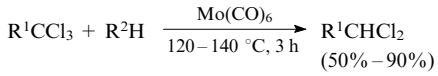
Scheme 131



R = Cl, Me; Red = $BH_3 \cdot$THF or 

A series of papers describe the reduction of the trichloromethyl group to the dichloromethyl group in the presence of $Mo(CO)_6$.[205 – 208] The hydrogen donors used in this reaction include isopropyl alcohol, cyclohexanol, n-butanethiol and triethylsilane (Scheme 132).

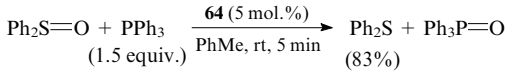
Scheme 132



R^1 = n-C_nH_{2n+1} (n = 5 – 8); R^2 = Pr^iO, CyO, Bu^nS, Et_3Si

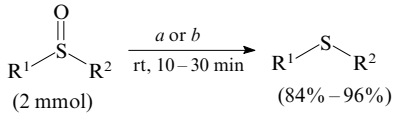
In the presence of $MoO(O_2)(phox)_2$ (**64**) in toluene, triphenylphosphine reduces diphenyl sulfoxide to diphenyl sulfide (Scheme 133).[101]

Scheme 133

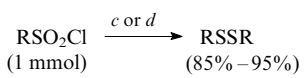


The $MoCl_5-NaI-MeCN$ and $MoCl_5-Zn-THF$ systems actively reduce sulfoxides to sulfides under mild conditions (20 °C, 30 min).[209] Under similar conditions, sulfonyl chlorides are reduced to disulfides. This method is general for a broad range of sulfoxides and sulfonyl chlorides (Scheme 134).

Scheme 134



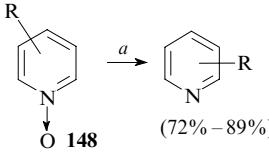
$R^1 = R^2$ = Ph, Bu^n; R^1 = Ph: R^2 = Me, Pr^n, Pr^i, Bu^n, Bn;
R^1 = Bn, R^2 = OMe;
(*a*) $MoCl_5-NaI-MeCN$ (1.4 mmol – 10 mmol – 20 ml);
(*b*) $MoCl_5-Zn-THF$ (1.2 mmol – 3 mmol – 10 ml)



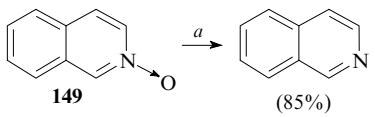
R = Ph, 4-MeC_6H_4, 4-BrC_6H_4, Me;
(*c*) $MoCl_5-NaI-MeCN$ (1.2 mmol – 10 mmol – 20 ml);
(*d*) $MoCl_5-Zn-THF$ (0.8 mmol – 3 mmol – 10 ml)

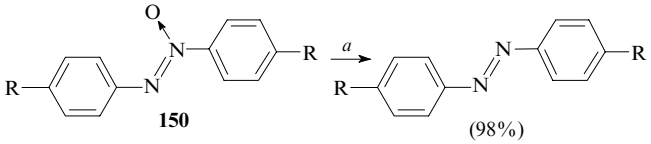
Molybdenum dichloride dioxide catalyzes deoxygenation of N-oxides **148**, **149** and nitrones **150** on treatment with PPh_3, which serves as the oxygen acceptor (Scheme 135).[210]

Scheme 135



R = 2-Me, 3-Me, 4-Me, 2-OH, 2-Br, 4-NO_2, 2-CO_2H, *etc.*

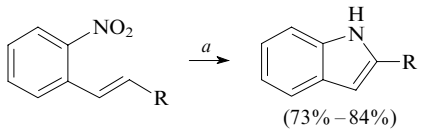




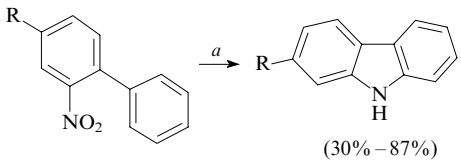
R = H, Me;
(*a*) PPh_3, MoO_2Cl_2, THF, 65 °C, 10 h; $-P(O)Ph_3$

Using MoO_2Cl_2, a number of indoles and carbazoles have been synthesized by reductive cyclization of aromatic nitro compounds in the presence of triphenylphosphine as the oxygen acceptor.[211] The reaction proceeds on refluxing in toluene and is completed in 16 – 24 h. The yields of indoles and carbazoles are moderate to high (Scheme 136).

Scheme 136



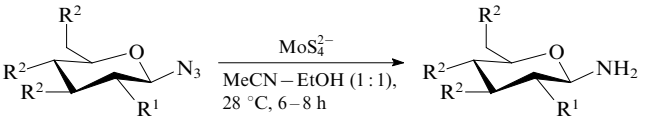
R = Me, n-C_5H_{11}, Ph, CO_2Me



R = H, F, OMe, CHO, Ac, CO_2Et, CO_2H;
(*a*) PPh_3 (2 equiv.), MoO_2Cl_2 (5 mol.%), PhMe, Δ, 16 – 24 h

The tetrathiomolybdate anion taken in a stoichiometric amount smoothly reduces β-D-glycosyl azides to the corresponding amines,[212] without affecting the polar substituents (BzO, BnO, AcO, AcNH) (Scheme 137).

Scheme 137

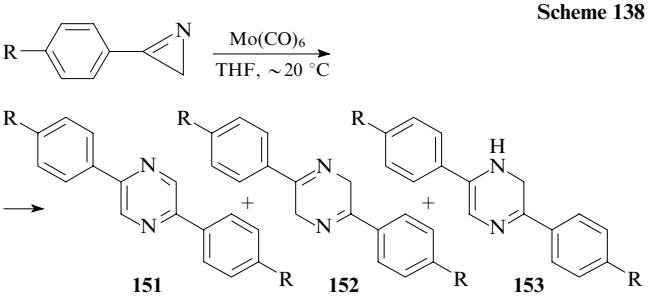


$R^1 = R^2$ = OAc (96% yield), OBz (96%), OBn (92%);
R^2 = OAc: R^1 = NHAc (92%), H (94%);
[azide] : [MoS_4^{2-}] = 1 : 1

XV. Catalysis of azirine reactions

Under the action of $Mo(CO)_6$, 2-arylazirines are converted to diarylpyrazines **151** and isomeric dihydropyrazines **152** and **153** (Scheme 138).[213]

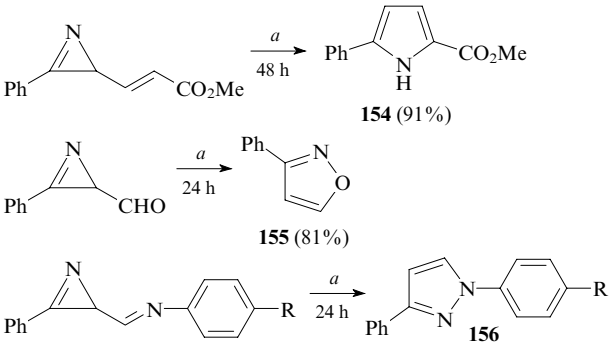
Scheme 138



R	Yield (%)		
	151	**152**	**153**
H	44	16	18
OMe	40	28	21
Me	27	21	40

The conversion route of azirines in the presence of $Mo(CO)_6$ depends on the nature of the substituent bound to the three-membered ring.[213] When functional groups such as C=C, C=O and C=N are present in the azirine moiety, the major reaction route is skeletal isomerization, resulting in the pyrrole (**154**), isoxazole (**155**) and pyrazole (**156**) derivatives (Scheme 139).

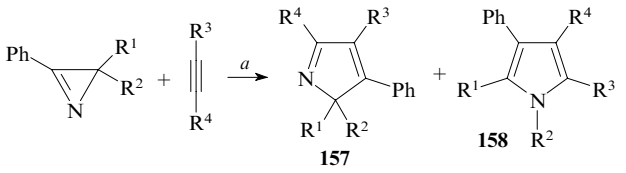
Scheme 139



R = H (73% yield), Cl (67%), Me (75%), OMe (96%);
(*a*) $Mo(CO)_6$, THF, ~20 °C

Inada *et al.*[214] described the reaction of 2-substituted 3-phenyl-2*H*-azirines with alkyl acetylene-carboxylates and -dicarboxylates in the presence of $Mo(CO)_6$. This reaction affords 2*H*-pyrrole (**157**) or pyrrole (**158**) derivatives (Scheme 140).

Scheme 140

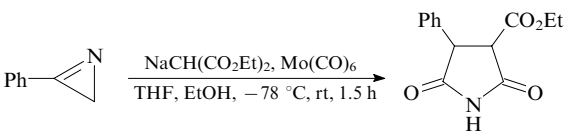


(*a*) $Mo(CO)_6$, C_6H_6, 35 – 50 °C, 3 days

R^1	R^2	R^3	R^4	Yield (%)	
				157	**158**
Me	Me	CO_2Me	CO_2Me	28	–
Me	Me	CO_2Et	CO_2Et	20	–
Me	Me	CO_2Me	H	5	–
Ph	H	CO_2Me	CO_2Me	–	20

The reaction of 3-phenyl-2*H*-azirine with sodium diethyl malonate in the presence of molybdenum hexacarbonyl results in the formation of pyrrolidine-2,5-dione (Scheme 141).[215]

Scheme 141

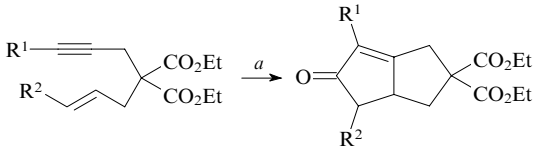


[azirine] : [malonate] : [Mo] = 1 : 1.5 : 1 (46%)

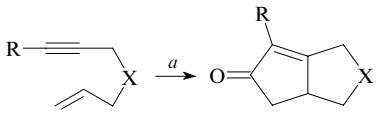
XVI. $Mo(CO)_6$-Mediated Pauson – Khand reaction

In a number of studies, molybdenum hexacarbonyl has been used as a catalyst and CO donor in the Pauson – Khand reaction.[216 – 220] This reaction is general for molybdenum, chromium and tungsten hexacarbonyls activated by promoters of various nature (*N*-methylmorpholine oxide, DMSO, dithiane or MeCN). The $Mo(CO)_6$ – DMSO system is most efficient. Under optimal conditions (100 °C, 12 h), the Pauson – Khand reaction can be carried out in the presence of $Mo(CO)_6$ – DMSO for a variety of enynes, in particular, the intermolecular version of the process is possible. Since $Mo(CO)_6$ serves as the source of CO, it is taken in a stoichiometric amount (Scheme 142).[216]

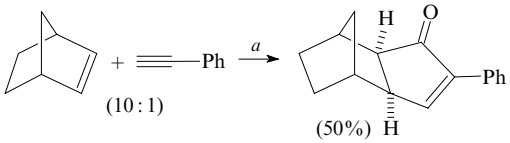
Scheme 142



R^2 = H: R^1 = H (76% yield), Me (80%); R^1 = H, R^2 = CH_2OBn (62%)



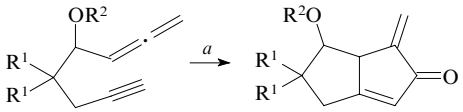
R = Ph, X = O (65% yield); R = H, X = NTs (69%)



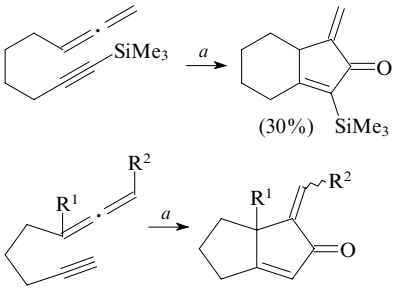
(*a*) $Mo(CO)_6$, DMSO, PhMe, 100 °C, 12 h

The $Mo(CO)_6$ – DMSO system actively catalyzes the Pauson – Khand reaction of allenes.[217 – 220] The reaction proceeds as [2 + 2 + 1] addition to give α-methylene- and α-alkylidene cyclopentenones (Scheme 143).

Scheme 143



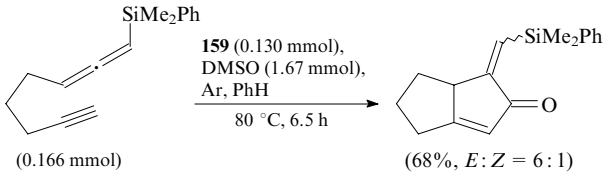
R^1 = R^2 = H (68% yield); R^1 = Me: R^2 = H (47%), $MeOCH_2$ (54%)



R^1 = H: R^2 = n-C_7H_{15} (75% yield, *E* : *Z* = 2 : 1),
Ph (70%, *E* : *Z* = 5 : 1); R^1 = Bu^n: R^2 = H (60%), $SiMe_3$ (59%);
(*a*) $Mo(CO)_6$, DMSO, PhMe, Ar, 110 °C, 10 h

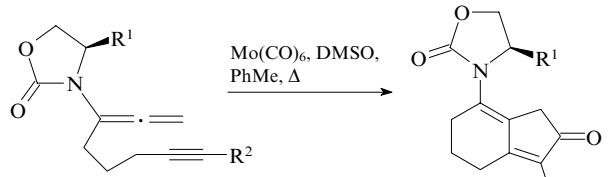
It is noteworthy that molybdenum hexacarbonyl, being a more efficient catalyst for Pauson – Khand cyclization of allenes than the cobalt alkyl complex or $(\eta^5\text{-Cp})_2ZrCl_2$, provides higher product yields, but it is considerably inferior to the zirconium and cobalt complexes in the stereoselectivity. The use of $Mo(CO)_3(\eta^6\text{-MesH})$ (**159**) (MesH = 1,3,5-$Me_3C_6H_3$) in this reaction made it possible to lower the reaction temperature to 80 °C and to conduct the reaction in benzene (Scheme 144).[220]

Scheme 144

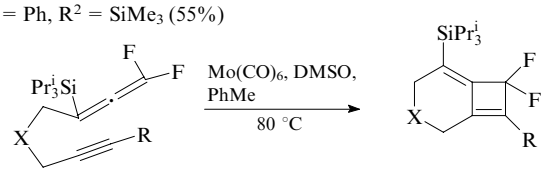


The Pauson – Khand reaction was carried out as intramolecular cycloaddition in the presence of $Mo(CO)_6$ for allenamines,[221] fluoroallenes[222] (Scheme 145) and bisallene-bisalkynes.[223]

Scheme 145



R^1 = H: R^2 = H (50% yield), $SiMe_3$ (59%);
R^1 = Ph, R^2 = $SiMe_3$ (55%)



X = $C(CO_2Et)$: R = H (81% yield), Me (72%), Pr^n (88%), Ph (75%);
X = NTs: R = H (86%), Me (92%), Pr^n (81%)

Alkynols, for example, alcohols **160** undergo $Mo(CO)_5(NEt_3)$-induced cyclization to give furan derivatives (Scheme 146).[224] Similar reactions can be conducted for epoxide **161** generated from 1-ethynylcyclohexene and for epoxyalkynes **162** – **164**, which are obtained from alkynols (see Scheme 146).

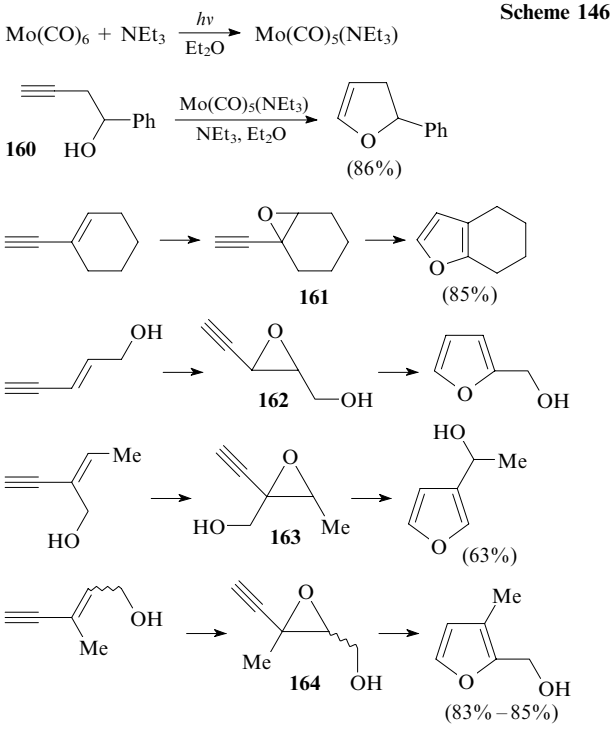
XVII. Aminocarbonylation of halo derivatives

A number of studies are devoted to the application of $Mo(CO)_6$ as a carbon oxide donor in the synthesis of amides from amines and aryl halides under the action of palladium complexes (Scheme 147).[225 – 233]

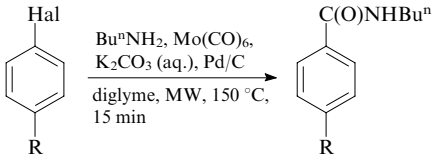
Palladium-catalyzed aminocarbonylation of various aryl and hetaryl halides with $Mo(CO)_6$ as a source of CO proceeds best of all in the presence of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) as a base. Microwave radiation increases the conversion of halides and reduces the reaction time to 10 min (Scheme 148).[234]

The synthesis of *N*(1),*N*(6)-bis(1*S*,2*R*)-2-hydroxy-1-indanyl-(2*R*,3*R*,4*R*,5*R*)-3,4-dihydroxy-2,5-bis(2-phenylcarbamoylbenzyloxy)hexane-1,6-diamide (**165**) — a HIV protease inhibitor — has been reported. Compound **165** contains four amide moieties, two of which have been

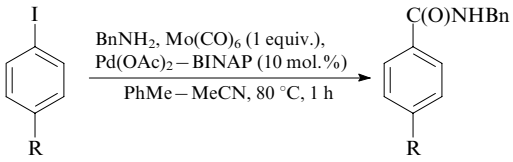
Scheme 146



Scheme 147

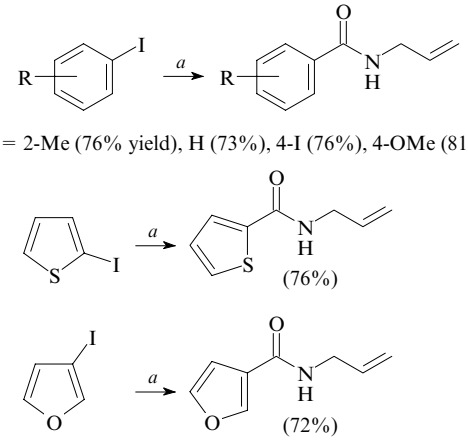


Hal = Br: R = OMe (70% yield), Me (71%), CF_3 (75%), Ac (77%);
Hal = I: R = OMe (69%), Me (72%), CF_3 (78%), Ac (79%)



R = OMe (63% yield), H (47%), CO_2Et (88%);
BINAP is 2,2′-bis(diphenylphosphino)binaphthyl

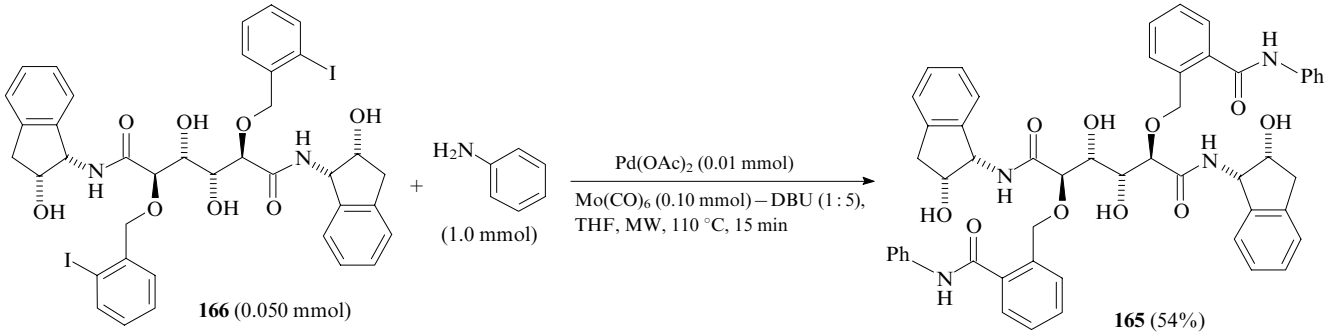
Scheme 148



R = 2-Me (76% yield), H (73%), 4-I (76%), 4-OMe (81%)

(*a*) $AllNH_2$, $Mo(CO)_6$ – DBU (1 : 3), $Pd(OAc)_2$ (7 mol.%), MW, 125 °C, 10 min

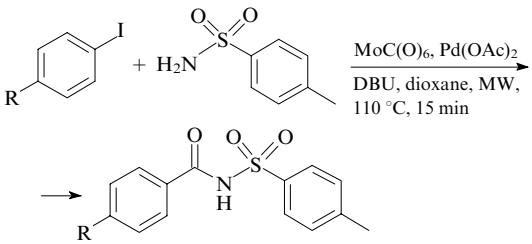
Scheme 149



constructed by the aminocarbonylation reaction involving iodoaryl moieties of the starting compound **166** and aniline (Scheme 149).[235]

Sulfonamides, for example, *p*-toluenesulfonamide, react with iodoaryls and $Mo(CO)_6$ to give the corresponding acylated derivatives (Scheme 150).[236]

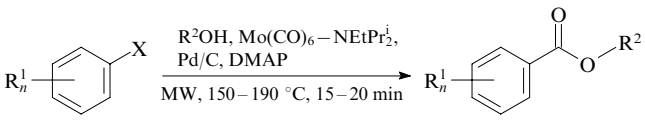
Scheme 150



R = OMe (88% yield), Me (87%), H (80%), Bz (70%), CF_3 (76%)

Molybdenum hexacarbonyl can serve as a CO donor in the synthesis of esters by the reaction of alcohols with aryl halides induced by Pd catalysts (Scheme 151).[237]

Scheme 151

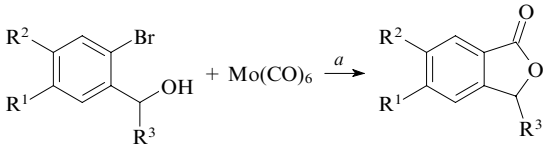


[ArX] : [Mo(CO)$_6$] : [Pd] : [NEtPr^i_2] : [DMAP] = 1 : 0.5 : 0.05 : 2 : 2; DMAP is 4-dimethylaminopyridine

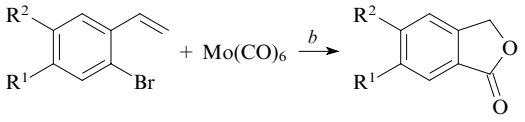
R^1_n	R^2	Yield (%)	
		X = I	X = Br
2,3-Benzo	Bu^n	89	64
4-OMe	Bu^n	63	72
2,3-Benzo	$(CH_2)_2SiMe_3$	86	–
2,3-Benzo	Bn	76	–
4-OMe	$(CH_2)_2SiMe_3$	74	–
4-OMe	Bn	74	–

The reaction of *o*-bromobenzyl alcohols[238] and *o*-bromostyrenes[239] with $Mo(CO)_6$ in the presence of Pd catalysts proceeds in a similar way. In this case, lactones are formed as the reaction products (Scheme 152).

Scheme 152



[substrate] : [Mo(CO)$_6$] : [Pd(OAc)$_2$] : [dppf] : [DMAP] : [NEtPr^i_2] = 20 : 10 : 1 : 1 : 40 : 40 (dppf is 1,1′-bis(diphenylphosphino)ferrocene; $R^1 = R^2 = R^3$ = H: (88% yield), Me (75%), F (77%); $R^2 = R^3$ = H: R^1 = Me (90%), OMe (84%), Cl (76%); $R^1 = R^2$ = OMe, R^3 = H (52%); (*a*) Pd(OAc)$_2$ – dppf, DMAP, NEtPr^i_2, dioxane;

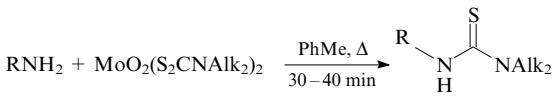


$R^1 = R^2$ = H (75% yield), OMe (59%); R^1 = Me, R^2 = H (77%); R^1 = H, R^2 = F (79%); (*b*) Pd(OAc)$_2$ – Bu^t_3PHBF$_4$, Bu^n_4NCl, PyH, dioxane, MW

XVIII. 'Unusual' reactions involving molybdenum compounds and complexes

Refluxing of amines with a stoichiometric amount of $MoO_2(S_2CNAlk_2)_2$ (Alk = Me, Et) in toluene affords substituted thioureas possessing fungicidal, herbicidal and antibacterial properties (Scheme 153).[240]

Scheme 153

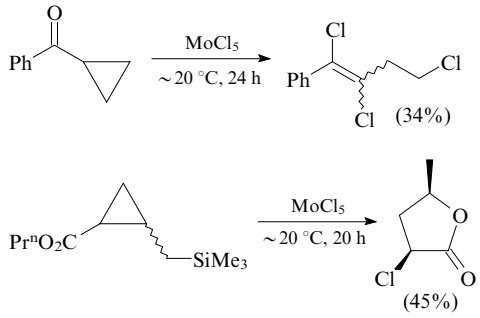


Alk = Et: R = Bn (72% yield), PhMeCH (68%), Cy (66%), Hex (85%); Alk = Me: R = Bn (62%), Cy (54%)

Molybdenum pentachloride reacts with cyclopropane-containing compounds — phenyl cyclopropyl ketone and propyl 2-(trimethylsilylmethyl)cyclopropanecarboxylate — along an intricate route. The reaction is accompanied by opening of a three-carbon ring and chlorination (Scheme 154).[241]

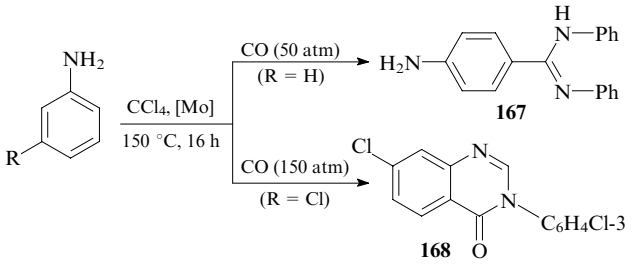
In the presence of molybdenum carbonyl complexes, $Mo(CO)_6$ and $(\eta^5\text{-}Cp)_2Mo_2(CO)_6$, non-trivial reactions of anilines with CCl_4 and the CCl_4 + CO system take place to give benzamidine **167** and quinazolin-4-one **168**

Scheme 154



(Scheme 155).[242] It is noteworthy that quinazolinones **168** are formed as the major products only in the case of substituted anilines.

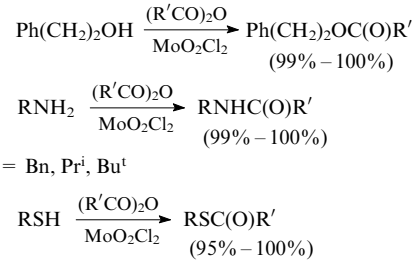
Scheme 155



For **167**: [Mo] = $(\eta^5\text{-Cp})_2Mo_2(CO)_6$ (89% yield), $Mo(CO)_6$ (94%); for **168**: [Mo] = $(\eta^5\text{-Cp})_2Mo_2(CO)_6$ (83%), $Mo(CO)_6$ (82%)

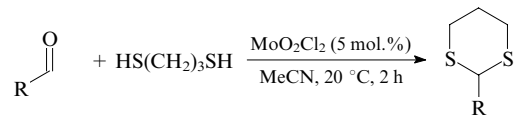
The high Lewis acidity inherent in MoO_2Cl_2 accounts for its activity towards acylation of alcohols, amines and thiols with acid anhydrides (Scheme 156).[243]

Scheme 156



Yet another reaction in which the acidic nature of MoO_2Cl_2 is manifested is the addition of propane-1,3-dithiol to aldehydes to give cyclic dithioacetals (Scheme 157).[244]

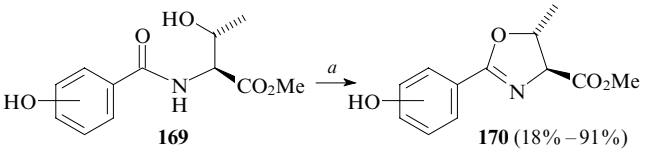
Scheme 157



R = Het, Ar, Alk

Ammonium molybdate catalyzes the intramolecular dehydration of N-acylthreonine derivatives **169**.[245] The reaction proceeds in the presence of a promoter, pentafluorobenzoic acid, and results in the formation of oxazolines **170** (Scheme 158).

Scheme 158

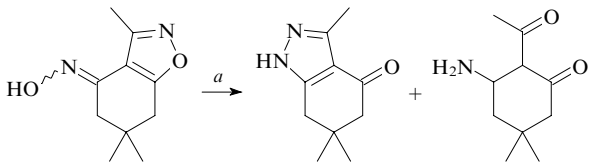


(*a*) $(NH_4)_2MoO_4 - C_6F_5CO_2H$, PhMe – DMF (9 : 1), azeotropic distillation, 1 – 10 h

Optically pure (4*S*,5*R*)-2-(2-hydroxyphenyl)-5-methyloxazoline-4-carboxylate (**170a**) obtained in this way was used for the total synthesis of the highly efficient anticancer agent BE-70016 (**171**), which was isolated previously from marine organisms (Scheme 159).[245]

Fused isoxazole **172** undergoes a complex transformation on heating in the presence of $Mo(CO)_6$ to furnish two compounds **173** and **174**. Pyrazole **173** is formed upon elimination of water and formation of a new ring; the participation of water in the formation of amino diketone **174** consists, most likely, in hydrolysis (Scheme 160).[246]

Scheme 160



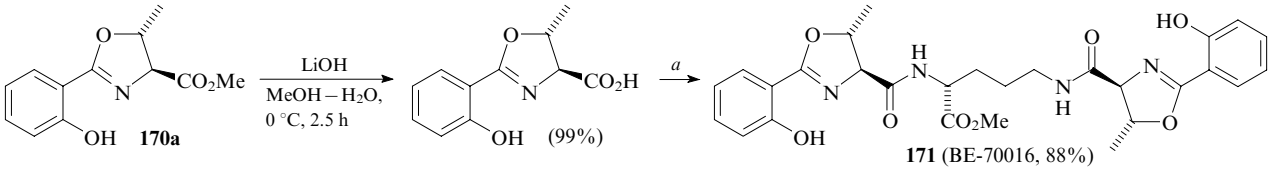
(*E*- and *Z*-isomer mixture, 1.69 mmol)

(~ 93% conversion, 1 : 2)

(*a*) $Mo(CO)_6$ (1.34 mmol), $MeCN - H_2O$ (1 : 6), Δ, 2 h

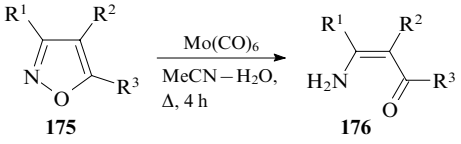
Refluxing of isoxazoles **175** under similar conditions in a water – acetonitrile mixture in the presence of $Mo(CO)_6$ affords β-aminoenones **176** (Scheme 161).[247 – 249]

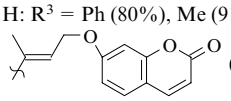
Scheme 159



(*a*) H_2N (CO2Me) NH_2, WSCI · HCl, HOBt, NEt_3, 6 °C, 15 h [WSCI · HCl is 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, HOBt is 1-hydroxybenzotriazole]

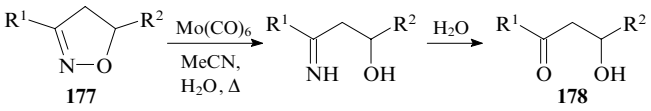
Scheme 161

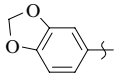


[substrate] : [Mo] = 2 : 1; R^1 = Ph: R^2 = H, R^3 = Ph (90% yield), $R^2 = R^3$ = H (91%), $R^2 - R^3 = (CH_2)_3$ (81%), $(CH_2)_4$ (77%); R^1 = Me, R^2 = H: R^3 = Ph (80%), Me (91%); $R^1 = CMe_2OH$, R^2 = H, R^3 =  (yield is not indicated)

Heating of 3,5-disubstituted isoxazolines **177** in aqueous acetonitrile in the presence of $Mo(CO)_6$ affords β-hydroxy ketones **178** (Scheme 162).[250]

Scheme 162

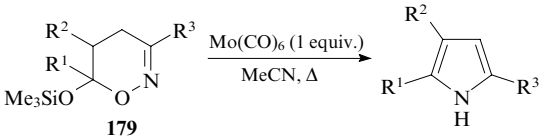


R^1	R^2	Yield of **178** (%)
CMe_2OH	n-C_8H_{17}	55
CMe_2OH	Bn	60
$(CH_2)_2CO_2Me$	n-$C_{10}H_{21}$	90
$(CH_2)_2CO_2H$	n-$C_{10}H_{21}$	80
$(CH_2)_2CO_2Me$	n-$C_{12}H_{25}$	90
Et	CH_2OTHP	92
	CMe_2OH	30
Hex	(*Z*)-CH=CHMe	70

4,5-Disubstituted isoxazolines can also be introduced in this reaction.[251]

In the presence of $Mo(CO)_6$, substituted 5,6-dihydro-4*H*-1,2-oxazines **179** are converted to substituted pyrroles **180** (Scheme 163).[252, 253]

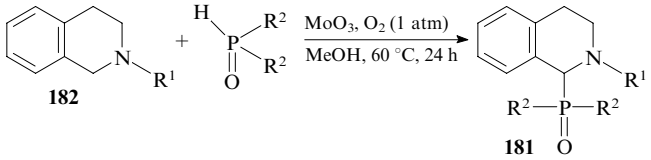
Scheme 163



R^1	R^2	R^3	Yield of **180** (%)
H	Me	Ph	69
Me	H	Ph	72
H	Me	CF_3	51
$(CH_2)_3$		Ph	41
$(CH_2)_4$		Ph	74
$(CH_2)_2CHBu^tCH_2$		Ph	51
$(CH_2)_4$		CO_2Et	70

Alagiri *et al.*[254] described the synthesis of α-aminophosphonates **181** by the reaction of *N*-aryltetrahydroisoquinolines **182** with dialkyl *H*-phosphonates under aerobic conditions in the presence of MoO_3 (Scheme 164).

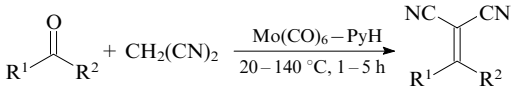
Scheme 164



[**182**] : [$HP(O)R^2_2$] : [MoO_3] = 1 : 1.1 : 0.05;
181: R^1 = Ph: R^2 = OEt (94% yield), OMe (87%);
$R^1 = C_6H_4OMe$-4: R^2 = OEt (90%), OMe (93%)

Pyridine-activated molybdenum hexacarbonyl catalyzes the condensation of malononitrile with ketones and aldehydes to yield alkylidenemalononitriles (Scheme 165).[255]

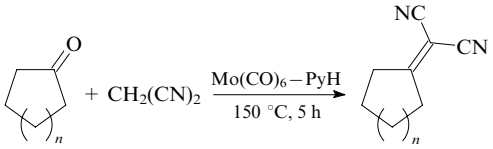
Scheme 165



R^1 = Me: R^2 = Me (98% yield), n-C_5H_{11} (95%), n-C_8H_{17} (98%), cyclo-C_3H_5 (98%), *etc.*

This reaction proceeds most smoothly with cyclic $C_5 - C_{12}$ ketones (Scheme 166).

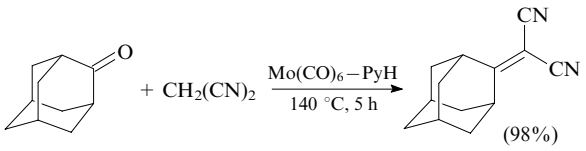
Scheme 166



n = 1 (99% yield), 2 (98%), 4 (75%), 8 (30%)

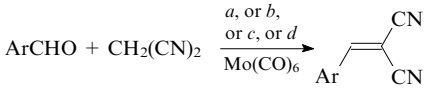
Adamantan-2-one also reacts rather actively with malononitrile (Scheme 167).

Scheme 167



The condensation of aromatic aldehydes with malononitrile proceeds under milder conditions: 20 – 40 °C, 5 min to 1 h (Scheme 168).

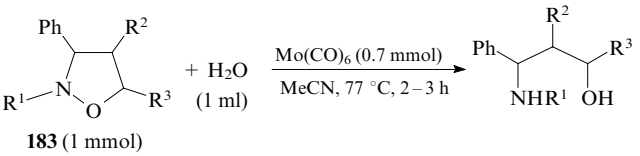
Scheme 168



(*a*) [Mo] – PyH (1 : 4), 20 °C, 5 min; Ar = Ph (99% yield);
(*b*) [Mo] – morpholine (1 : 4), 20 °C, 5 min; Ar = Ph;
(*c*) [Mo] – PyH (1 : 4), 40 °C, 1 h; Ar = 4-$Me_2NC_6H_4$ (98%), 4-$MeOC_6H_4$ (99%), 1-Naph (98%);
(*d*) [Mo] – morpholine (1 : 4), 40 °C, 1 h; Ar = 1-Naph

Isoxazolidines **183** react with water under the action of $Mo(CO)_6$ to be converted to the corresponding amino alcohols (Scheme 169).[256]

Scheme 169

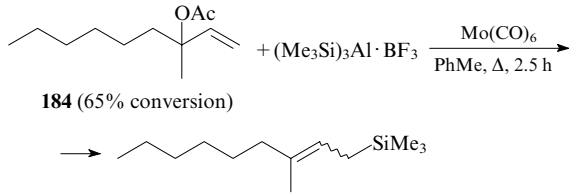


183 (1 mmol)

R^1	R^2	R^3	Yield (%)
Me	H	Pr^n	78
Ph	H	Ph	85
Ph	CO_2Me	Me	88
Me	$(CH_2)_3$		11

Molybdenum hexacarbonyl catalyzes the exchange reaction between 3-acetoxy-3-methylnon-1-ene (**184**) and $(Me_3Si)_3Al \cdot BF_3$ (Scheme 170).[257]

Scheme 170



184 (65% conversion)

(100%, $E:Z = 2:1$)

It is worth noting that $Mo(CO)_6$ favours the introduction of the silyl group into the less hindered position, unlike palladium complexes used as catalysts.

* * *

The material summarized in the review illustrates the extensive potential of molybdenum compounds and complexes in the catalysis and organic synthesis and, in our opinion, would draw attention of researchers and chemical engineers to this obviously interesting and promising area of organic chemistry. A characteristic feature and benefit of molybdenum catalysts is high activity, irrespective of the metal oxidation state. In most reactions, no auxiliary reagents, in particular, no reducing agents are needed to transform molybdenum compounds into catalytically active species.

In our opinion, for increasing the activity and the scope of applicability of molybdenum catalysts, it is necessary to use more efficient activating ligands, to conduct reactions in supercritical media or ionic liquids and to employ immobilized catalyst forms.

References

1. N N Tomina, A A Pimerzin, I K Moiseev *Russ. J. Gen. Chem.* **79** 1274 (2009)
2. R R Schrock, A Hoveyda *Angew. Chem., Int. Ed.* **42** 4592 (2003)
3. *Handbook of Metathesis. Catalyst Development and Mechanism* Vol. 1 (2nd Edn) (Eds R H Grubbs, A G Wenzel) (Wiley-VCH, 2015)
4. *New Trends in the Chemistry of Nitrogen Fixation* (Eds J Chatt, L M Camara Pina, R Richards) (London: Academic Press, 1980)
5. A E Shilov *Metal Complexes in Biometric Chemical Reactions* (Boca Raton, FL: CRC Press, 1997)
6. J M Khurana, S Chauhan, A Agrawal *Org. Prep. Proced. Int.* **36** 201 (2004)
7. F E Kühn, A M Santos, M Abrantes *Chem. Rev.* **106** 2455 (2006)
8. J Sobczak, J J Ziółkowski *J. Mol. Catal.* **13** 11 (1981)
9. C Freund, M Abrantes, F E Kühn *J. Organomet. Chem.* **691** 3718 (2006)
10. M D Curtis *J. Cluster Sci.* **7** 247 (1996)
11. G A Tolstikov, V P Yur'ev, U M Dzhemilev *Russ. Chem. Rev.* **44** 319 (1975)
12. G A Tolstikov *Reaktsii Gidroperekisnogo Okisleniya* (Reactions of Hydrogen Peroxide Oxidation) (Moscow: Nauka, 1976)
13. K Jeyakumar, D K Chand *J. Chem. Sci.* **121** 111 (2009)
14. R G de Noronha, A C Fernandes *Curr. Org. Chem.* **16** 33 (2012)
15. B M Trost, M L Crawley *Chem. Rev.* **103** 2921 (2003)
16. O Belda, C Moberg *Acc. Chem. Res.* **37** 159 (2004)
17. B M Trost *Org. Process Res. Dev.* **16** 185 (2012)
18. S C A Sousa, I Cabrita, A C Fernandes *Chem. Soc. Rev.* **41** 5641 (2012)
19. Q-H Xia, H-Q Ge, C-P Ye, Z-M Liu, K-X Su *Chem. Rev.* **105** 1603 (2005)
20. A J Burke *Coord. Chem. Rev.* **252** 170 (2008)
21. M Amini, M M Haghdoost, M Bagherzadeh *Coord. Chem. Rev.* **257** 1093 (2013)
22. *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis* (Ed. S T Oyama) (Elsevier, 2011)
23. N Indictor, W F Brill *J. Org. Chem.* **30** 2074 (1965)
24. M Sheng, J Zajacek, in *International Oxidation Symposium (Proceedings) San-Francisco, CA, 1967* p. 243
25. R A Sheldon, J A Van Doorn *J. Catal.* **31** 427 (1973)
26. R A Sheldon, J A Van Doorn, C W A Schram, A J De Jong *J. Catal.* **31** 438 (1973)
27. Patent US 3351635 (1967); *Chem. Abstr.* **71** 81043 (1969)
28. U M Dzhemilev, V P Yur'ev, G A Tolstikov, F B Gershanov, S R Rafikov *Dokl. Akad. Nauk SSSR* **196** 588 (1971); *Chem. Abstr.* **74** 142171 (1971)
29. G A Tolstikov, U M Dzhemilev, V P Yur'ev *Zh. Org. Khim.* **8** 2204 (1972); *Chem. Abstr.* **78** 43834 (1973)
30. G A Tolstikov, U M Dzhemilev, V P Yur'ev, S R Rafikov *Dokl. Akad. Nauk SSSR* **208** 376 (1973); *Chem. Abstr.* **78** 159981 (1973)
31. U M Dzhemilev, V P Yur'ev, G A Tolstikov *Zh. Obshch. Khim.* **40** 2518 (1970); *Chem. Abstr.* **74** 125898 (1971)
32. V P Yur'ev, I A Gailyunas, Z G Isaeva, G A Tolstikov *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **28** 885 (1974)
33. Yu B Trach, O I Makota, M V Nikipanchuk, I Yu Pyrig, R G Makitra *Neftekhimiya* **43** 464 (2003); *Chem. Abstr.* **140** 341068 (2004)
34. Yu B Trach, O I Makota *Neftekhimiya* **45** 355 (2005); *Chem. Abstr.* **144** 212356 (2005)
35. Yu B Trach, M V Nikipanchuk, Z M Komarenskaya *Kinet. Catal.* **45** 504 (2004)
36. Yu B Trach, O I Makota *Neftekhimiya* **44** 52 (2004); *Chem. Abstr.* **141** 175798 (2004)
37. M Farias, M Martinelli, D P Bottega *Appl. Catal., A: Gen.* **384** 213 (2010)
38. S M Bruno, S S Balula, A A Valente, F A A Paz, M Pillinger, C Sousa, J Klinowski, C Freire, P Ribeiro-Claro, I S Gonçalves *J. Mol. Catal. A: Chem.* **270** 185 (2007)
39. R M Calvente, J M Campos-Martin, J L G Fierro *Catal. Commun.* **3** 247 (2002)
40. F-L Chai, X-Y Wang, X-R Zhang, J-C Tao *React. Kinet. Catal. Lett.* **97** 341 (2009)
41. J M Sobczak, J J Ziółkowski *Appl. Catal., A: Gen.* **248** 261 (2003)
42. V V K M Kandepi, J M S Cardoso, B Royo *Catal. Lett.* **136** 222 (2010)

43. M Abrantes, S M Bruno, C Tomé, M Pillinger, I S Gonçalves, A A Valente *Catal. Commun.* **15** 64 (2011)
44. T R Amarante, P Neves, C Tomé, M Abrantes, A A Valente, F A A Paz, M Pillinger, I S Gonçalves *Inorg. Chem.* **51** 3666 (2012)
45. B Monteiro, S S Balula, S Gago, C Grosso, S Figueiredo, A D Lopes, A A Valente, M Pillinger, J P Lourenço, I S Gonçalves *J. Mol. Catal. A: Chem.* **297** 110 (2009)
46. A Castro, J C Alonso, A A Valente, P Neves, P Brandão, V Félix, P Ferreira *Eur. J. Inorg. Chem.* 1405 (2010)
47. Z Petrovski, M Pillinger, A A Valente, I S Gonçalves, A Hazell, C C Romão *J. Mol. Catal. A: Chem.* **227** 67 (2005)
48. A A Valente, J Moreira, A D Lopes, M Pillinger, C D Nunes, C C Romão, F E Kühn, I S Gonçalves *New J. Chem.* **28** 308 (2004)
49. P Neves, S Gago, C C L Pereira, S Figueiredo, A Lemos, A D Lopes, I S Gonçalves, M Pillinger, C M Silva, A A Valente *Catal. Lett.* **132** 94 (2009)
50. P Neves, C C L Pereira, F A A Paz, S Gago, M Pillinger, C M Silva, A A Valente, C C Romão, I S Gonçalves *J. Organomet. Chem.* **695** 2311 (2010)
51. A A Valente, J D Seixas, I S Gonçalves, M Abrantes, M Pillinger, C C Romão *Catal. Lett.* **101** 127 (2005)
52. S M Bruno, C C L Pereira, M S Balula, M Nolasco, A A Valente, A Hazell, M Pillinger, P Ribeire-Claro, I S Gonçalves *J. Mol. Catal. A: Chem.* **261** 79 (2007)
53. M Abrantes, F A A Paz, A A Valente, C C L Pereira, S Gago, A E Rodrigues, J Klinowski, M Pillinger, I S Gonçalves *J. Organomet. Chem.* **694** 1826 (2009)
54. A Capapé, A Raith, E Herdtweck, M Cokoja, F E Kühn *Adv. Synth. Catal.* **352** 547 (2010)
55. A Capapé, A Raith, F E Kühn *Adv. Synth. Catal.* **351** 66 (2009)
56. M Vasconcellos-Dias, C D Nunes, P D Vaz, P Ferreira, P Brandão, V Félix, M J Calhorda *J. Catal.* **256** 301 (2008)
57. C I Fernandes, N U Silva, P D Vaz, T G Nunes, C D Nunes *Appl. Catal., A: Gen.* **384** 84 (2010)
58. D Betz, W A Herrmann, F Z Kühn *J. Organomet. Chem.* **694** 3320 (2009)
59. J A Brito, S Ladeira, E Teuma, B Royo, M Gómez *Appl. Catal., A: Gen.* **398** 88 (2011)
60. B Monterio, S Gago, P Neves, A A Valente, I S Gonçalves, C C L Pereira, C M Silva, M Pillinger *Catal. Lett.* **129** 350 (2009)
61. M Herbert, F Montilla, R Moyano, A Pastor, E Álvarez, A Galindo *Polyhedron* **28** 3929 (2009)
62. S M Bruno, B Monteiro, M S Balula, F M Pedro, M Abrantes, A A Valente, M Pillinger, P Ribeiro-Claro, F E Kühn, I S Gonçalves *J. Mol. Catal. A: Chem.* **260** 11 (2006)
63. A A Valente, I S Gonçalves, A D Lopes, J E Rodríguez-Borges, M Pillinger, C C Romão, J Rocha, X García-Mera *New J. Chem.* **25** 959 (2001)
64. S M Bruno, J A Fernandes, L S Martins, I S Gonçalves, M Pillinger, P Ribeiro-Claro, J Rocha, A A Valente *Catal. Today* **114** 263 (2006)
65. J Pisk, D Agustin, V Vrdoljak, R Poli *Adv. Synth. Catal.* **353** 2910 (2011)
66. S Krackl, A Company, S Enthaler, M Driess *ChemCatChem* **3** 1186 (2011)
67. G Chahboun, J A Brito, B Royo, M A El Amrani, E Gómez-Bengoa, M E G Mosquera, T Cuenca, E Royo *Eur. J. Inorg. Chem.* 2940 (2012)
68. W A Herrmann, J J Haider, J Fridgen, G M Lobmaier, M Spiegler *J. Organomet. Chem.* **603** 69 (2000)
69. I S Gonçalves, A M Santos, C S Romão, A D Lopes, J E Rodríguez-Borges, M Pillinger, P Ferreira, J Rocha, F E Kühn *J. Organomet. Chem.* **626** 1 (2001)
70. A M Santos, F E Kühn, K Bruus-Jensen, I Lucas, C C Romão, E Herdtweck *J. Chem. Soc., Dalton Trans.* 1332 (2001)
71. A C Coelho, M Nolasco, S S Balula, M M Antunes, C C L Pereira, A F A Paz, A A Valente, M Pillinger, P Ribeiro-Claro, J Klinowski, I S Gonçalves *Inorg. Chem.* **50** 525 (2011)
72. F E Kühn, M Groarke, É Bencze, E Herdtweck, A Prazeres, A M Santos, M J Calhorda, C C Romão, I S Gonçalves, A D Lopes, M Pillinger *Chem. – Eur. J.* **8** 2370 (2002)
73. A Al-Ajlouni, A A Valente, C D Nunes, M Pillinger, A M Santos, J Zhao, C C Romão, I S Gonçalves, F E Kühn *Eur. J. Inorg. Chem.* 1716 (2005)
74. J A Brito, H Teruel, G Muller, S Massou, M Gómez *Inorg. Chim. Acta* **361** 2740 (2008)
75. M Gómez, S Jansat, G Muller, G Noguera, H Teruel, V Moliner, E Cerrada, M Hursthouse *Eur. J. Inorg. Chem.* 1071 (2001)
76. J A Brito, M Gómez, G Muller, H Teruel, J-C Clinet, E Duñach, M A Maestro *Eur. J. Inorg. Chem.* 4278 (2004)
77. J A Brito, B Royo, M Gómez *Catal. Sci. Technol.* **1** 1109 (2011)
78. A U Barlan, W Zhang, H Yamamoto *Tetrahedron* **63** 6075 (2007)
79. A Rezaeifard, I Sheikhshoaie, N Monadi, H Stoeckli-Evans *Eur. J. Inorg. Chem.* 799 (2010)
80. A Günyar, D Betz, M Drees, E Herdtweck, F E Kühn *J. Mol. Catal. A: Chem.* **331** 117 (2010)
81. J Zhao, E Herdtweek, F E Kühn *J. Organomet. Chem.* **691** 2199 (2006)
82. M Abrantes, A Sakthivel, C C Romão, F E Kühn *J. Organomet. Chem.* **691** 3137 (2006)
83. P M Reis, C A Gamelas, J A Brito, N Saffon, M Gómez, B Royo *Eur. J. Inorg. Chem.* 666 (2011)
84. F E Kühn, A M Santos, A D Lopes, I S Gonçalves, J E Rodrígues-Borges, M Pillinger, C C Romão *J. Organomet. Chem.* **621** 207 (2001)
85. J Fridgen, W A Herrmann, G Eickerling, A M Santos, F E Kühn *J. Organomet. Chem.* **689** 2752 (2004)
86. J Zhao, X Zhou, A M Santos, E Herdtweck, C C Romão, F E Kühn *Dalton Trans.* 3736 (2003)
87. X-Y Wang, H-C Shi, C Sun, Z-G Zhang *Tetrahedron* **60** 10993 (2004)
88. A U Barlan, A Basak, H Yamamoto *Angew. Chem., Int. Ed.* **45** 5849 (2006)
89. G A Tolstikov, U M Dzhemilev, V P Yur'ev *Zh. Org. Khim.* **8** 1190 (1972); *Chem. Abstr.* **77** 10986 (1972)
90. A V Biradar, B R Sathe, S B Umbarkar, M K Dongare *J. Mol. Catal. A: Chem.* **285** 111 (2008)
91. M Bagherzadeh, M Amini, A Ellern, L K Woo *Inorg. Chem. Commun.* **15** 52 (2012)
92. R Bandyopadhyay, S Biswas, S Guha, A K Mukherjee, R Bhattacharyya *Chem. Commun.* 1627 (1999)
93. U M Dzhemilev, Candidate Thesis in Chemical Sciences, Bashkir State University, Ufa, 1972
94. G A Tolstikov, U M Dzhemilev, V P Yur'ev *Zh. Obshch. Khim.* **42** 1611 (1972); *Chem. Abstr.* **77** 114716 (1972)
95. S E Jacobson, D A Muccigrosso, F Mares *J. Org. Chem.* **44** 921 (1979)
96. Z Wang, C W Kee, S Li, T S A Hor, J Zhao *Appl. Catal., A: Gen.* **393** 269 (2011)
97. L Kuhnen *Angew. Chem., Int. Ed. Engl.* **5** 893 (1966)
98. G A Tolstikov, U M Dzhemilev, N N Novitskaya, V P Yur'ev, R G Kantyukova *Zh. Obshch. Khim.* **41** 1883 (1971); *Chem. Abstr.* **76** 3433 (1972)
99. G A Tolstikov, U M Dzhemilev, N N Novitskaya, V P Yur'ev *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **21** 2675 (1972)
100. R Sanz, R Aguado, M R Pedrosa, F J Arnáiz *Synthesis* 856 (2002)
101. M Bagherzadeh, M M Haghdoost, M Amini, P G Derakhshandeh *Catal. Commun.* **23** 14 (2012)
102. F Romano, A Linden, M Mba, C Zonta, G Licini *Adv. Synth. Catal.* **352** 2937 (2010)

103. C A Gamelas, T Lourenço, A Pontes da Costa, A L Simplício, B Royo, C C Romão *Tetrahedron Lett*. **49** 4708 (2008)
104. K Jeyakumar, D K Chand *Tetrahedron Lett*. **47** 4573 (2006)
105. H Sakuraba, H Maekawa *J. Inclusion Phenom. Macrocycl. Chem*. **54** 41 (2006)
106. A Basak, A U Barlan, H Yamamoto *Tetrahedron: Asymmetry* **17** 508 (2006)
107. J M Khurana, A Agrawal, S Kumar *J. Braz. Chem. Soc*. **20** 1256 (2009)
108. M N Sheng, J G Zajasek *J. Org. Chem*. **33** 588 (1968)
109. G A Tolstikov, U M Dzhemilev, V P Yur'ev *Zh. Org. Khim*. **8** 1186 (1972); *Chem. Abstr*. **77** 101425 (1972)
110. G A Tolstikov, U M Dzhemilev, V P Yur'ev *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **21** 638 (1972)
111. G A Tolstikov, U M Dzhemilev, V P Jurjev, F B Gershanov, S R Rafikov *Tetrahedron Lett*. 2807 (1971)
112. U M Dzhemilev, N S Vostrikov, G A Tolstikov, S R Rafikov *Dokl. Akad. Nauk. SSSR* **244** 369 (1979); *Chem. Abstr*. **90** 137295 (1979)
113. M Maddani, K R Prabhu *Tetrahedron Lett*. **49** 4526 (2008)
114. A V Biradar, T V Kotbagi, M K Dongare, S B Umbarkar *Tetrahedron Lett*. **49** 3616 (2008)
115. S Tollari, M Cuscela, F Porta *J. Chem. Soc., Chem. Commun*. 1510 (1993)
116. S Tollari, S Bruni, C L Bianchi, M Rainoni, F Porta *J. Mol. Catal*. **83** 311 (1993)
117. F Porta, L Prati *J. Mol. Catal. A: Chem*. **157** 123 (2000)
118. F J Arnaiz, R Aguado, J M Martinez-Ilarduya *Polyhedron* **13** 3257 (1994)
119. R I Khusnutdinov, N A Shchadneva, R Yu Burangulova, Z S Muslimov, U M Dzhemilev *Russ. J. Org. Chem*. **42** 1615 (2006)
120. R I Khusnutdinov, N A Shchadneva, A R Baiguzina, Yu Yu Lavrent'eva, R Yu Burangulova, A M Atnabaeva, U M Dzhemilev *Neftekhimiya* **44** 380 (2004); *Chem. Abstr*. **142** 463330 (2004)
121. R I Khusnutdinov, N A Shchadneva, A R Bayguzina, T M Oshnyakova, Yu Yu Mayakova, U M Dzhemilev *Russ. J. Org. Chem*. **49** 1557 (2013)
122. Patent RF 2287515 (2006); *Chem. Abstr*. **145** 507471 (2006)
123. R I Khusnutdinov, N A Shchadneva, R Yu Burangulova, T M Oshnyakova, U M Dzhemilev *Russ. J. Org. Chem*. **43** 623 (2007)
124. R I Khusnutdinov, N A Shchadneva, L F Mukhametshina, U M Dzhemilev *Russ. J. Org. Chem*. **45** 1137 (2009)
125. R Yu Burangulova, Candidate Thesis in Chemical Sciences, Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, Ufa, 2006
126. Patent RF 2286332 (2006); *Chem. Abstr*. **145** 454780 (2006)
127. Patent RF 2342358 (2008); *Chem. Abstr*. **150** 55724 (2008)
128. R I Khusnutdinov, N A Shchadneva, T M Oshnyakova, U M Dzhemilev *Petrol. Chem*. **51** 435 (2011)
129. Patent RF 2384566 (2010); *Chem. Abstr*. **152** 334877 (2010)
130. Patent RF 2420506 (2009)
131. H Alper, D Des Roches, T Durst, R Legault *J. Org. Chem*. **41** 3611 (1976)
132. S M Bruno, C A Gamelas, A C Gomes, A A Valente, M Pillinger, C C Romão, I S Gonçalves *Catal. Commun*. **23** 58 (2012)
133. A Patra, M Bandyopadhyay, D Mal *Tetrahedron Lett*. **44** 2355 (2003)
134. L Hills, R Moyano, F Montilla, A Pastor, A Galindo, E Álvares, F Marchetti, C Pettinari *Eur. J. Inorg. Chem*. 3352 (2013)
135. K Jeyakumar, D K Chand *Synthesis* 807 (2008)
136. J R Dethlefsen, D Lupp, B-C Oh, P Fristrup *ChemSusChem* **7** 425 (2014)
137. D Lupp, N J Christensen, J R Dethlefsen, P Fristrup *Chem. – Eur. J*. **21** 3435 (2015)
138. M Mba, M Pontini, S Lovat, C Zonta, G Bernardinelli, P E Kündig, G Licini *Inorg. Chem*. **47** 8616 (2008)
139. R I Khusnutdinov, N A Shchadneva, A R Baiguzina, Yu Yu Lavrent'eva, R Yu Burangulova, U M Dzhemilev *Neftekhimiya* **44** 148 (2004); *Chem. Abstr*. **141** 349834 (2004)
140. R I Khusnutdinov, N A Shchadneva, A R Baiguzina, Yu Yu Lavrent'eva, R Yu Burangulova, U M Dzhemilev *Neftekhimiya* **44** 293 (2004); *Chem. Abstr*. **142** 6254 (2004)
141. R Kh Freidlina, F K Velichko, S S Zlotskii, D L Rakhmankulov, A B Terent'ev *Radikal'naya Telomerizatsiya* (Radical Telomerization) (Moscow: Khimiya, 1988)
142. B Boualy, M A Harrad, L El Firdoussi, M A Ali, S El Houssame, A Karim *Catal. Commun*. **12** 1295 (2011)
143. Y Shvo, R Green *J. Organomet. Chem*. **675** 77 (2003)
144. Patent RF 2331627 (2007)
145. R Davis, I F Groves *J. Chem. Soc., Dalton Trans*. 2281 (1982)
146. T Susuki, J Tsuji *J. Org. Chem*. **35** 2982 (1970)
147. Y Mori, J Tsuji *Tetrahedron* **28** 29 (1972)
148. C Moberg *Org. React*. **84** 1 (2014)
149. B M Trost, M Lautens *J. Am. Chem. Soc*. **104** 5543 (1982)
150. B M Trost, M Lautens *J. Am. Chem. Soc*. **105** 3343 (1983)
151. B M Trost, M Lautens *Organometallics* **2** 1687 (1983)
152. B M Trost, I Hachiya *J. Am. Chem. Soc*. **120** 1104 (1998)
153. B M Trost, Y Zhang *J. Am. Chem. Soc*. **128** 4590 (2006)
154. B M Trost, Y Zhang *J. Am. Chem. Soc*. **129** 14548 (2007)
155. N-F K Kaiser, U Bremberg, M Larhed, C Moberg, A Hallberg *Angew. Chem., Int. Ed*. **39** 3595 (2000)
156. M Palucki, J M Um, D A Conlon, N Yasuda, D L Hughes, B Mao, J Wang, P J Reider *Adv. Synth. Catal*. **343** 46 (2001)
157. O Belda, N-F Kaiser, U Bremberg, M Larhed, A Hallberg, C Moberg *J. Org. Chem*. **65** 5868 (2000)
158. B M Trost, M Osipov, S Krüger, Y Zhang *Chem. Sci*. **6** 349 (2015)
159. A Srivastava, Y-A Ma, R Pankayatselvan, W Dinges, K M Nicholas *J. Chem. Soc., Chem. Commun*. 853 (1992)
160. R S Srivastava, K M Nicholas *J. Org. Chem*. **59** 5365 (1994)
161. T J Chow, L-K Liu, Y-S Chao *J. Chem. Soc., Chem. Commun*. 700 (1985)
162. T J Chow, Y-S Chao, L-K Liu *J. Am. Chem. Soc*. **109** 797 (1987)
163. T J Chow, M-Y Wu, L-K Liu *J. Organomet. Chem*. **281** c33 (1985)
164. T J Chow, Y-S Chao *J. Organomet. Chem*. **296** c23 (1985)
165. T Schmidt, F Bienewald, R Goddard *J. Chem. Soc., Chem. Commun*. 1857 (1994)
166. Patent RF 2378243 (2010); *Chem. Abstr*. **152** 97163 (2010)
167. R Hara, Q Guo, T Takahashi *Chem. Lett*. 140 (2000)
168. K S Choi, M K Park, B H Han *Bull. Korean Chem. Soc*. **19** 1257 (1998)
169. G A Ardizzoia, S Brenna, G LaMonica, A Maspero, N Masciocchi *J. Organomet. Chem*. **649** 173 (2002)
170. T Sugihara, M Yamada, M Nishizawa *J. Indian Chem. Soc*. **75** 645 (1998)
171. R I Khusnutdinov, N A Shchadneva, L F Mukhametshina, U M Dzhemilev *Russ. J. Org. Chem*. **44** 1084 (2008)
172. Patent RF 2316540 (2008); *Chem. Abstr*. **148** 214774 (2008)
173. R I Khusnutdinov, N A Shchadneva, L F Khisamova, Yu Yu Mayakova, U M Dzhemilev *Russ. J. Org. Chem*. **47** 1898 (2011)
174. Patent RF 2401828 (2010); *Chem. Abstr*. **153** 529919 (2010)
175. K Alagiri, K R Prabhu *Org. Biomol. Chem*. **10** 835 (2012)
176. I Shimizu, K M Khien, M Nagatomo, T Nakajima, A Yamamoto *Chem. Lett*. 851 (1997)
177. R G de Noronha, A C Fernandes, C C Romão *Tetrahedron Lett*. **50** 1407 (2009)
178. R I Khusnutdinov, N A Shchadneva, A R Baiguzina, R R Mukminov, Yu Yu Mayakova, A A Smirnov, U M Dzhemilev *Petrol. Chem*. **48** 471 (2008)
179. R I Khusnutdinov, N A Shchadneva, A R Bayguzina, Yu Yu Mayakova, A A Smirnov, R Yu Burangulova, U M Dzhemilev *Arkivos* (xi) 53 (2004)
180. K Jeyakumar, D K Chand *Synthesis* 1685 (2008)
181. M P Doyle, J G Davidson *J. Org. Chem*. **45** 1538 (1980)

182. I S Akhrem, N M Chistovalova, D V Avetisyan, V F Sizoi, M E Vol'pin *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **36** 1732 (1987)
183. T Hirao, S Kohno, Y Ohshiro, T Agawa *Bull. Chem. Soc. Jpn.* **56** 1569 (1983)
184. A D Calhoun, K R Lung, T A Nile, L L Stoke, S C Smith *Trans. Met. Chem.* **8** 365 (1983)
185. M Stosur, T Szymańska-Buzar *J. Mol. Catal. A: Chem.* **286** 98 (2008)
186. S Chakraborty, O Blacque, T Fox, H Berke *ACS Catal.* **3** 2208 (2013)
187. P J Costa, C C Romão, A C Fernandes, B Royo, P M Reis, M J Calhorda *Chem. – Eur. J.* **13** 3934 (2007)
188. P M Reis, C C Romão, B Royo *Dalton Trans.* 1842 (2006)
189. A C Fernandes, R Fernandes, C C Romão, R Boyo *Chem. Commun* 213 (2005)
190. A Y Khalimon, S K Ignatov, R Simionescu, L G Kuzmina, J A K Howard, G I Nikonov *Inorg. Chem.* **51** 754 (2012)
191. U Kazmaier, D Schauss, M Pohlman *Org. Lett.* **1** 1017 (1999)
192. U Kazmaier, M Pohlman, D Schauß *Eur. J. Org. Chem.* 2761 (2000)
193. S Braune, U Kazmaier *J. Organomet. Chem.* **641** 26 (2002)
194. H Lin, U Kazmaier *Eur. J. Org. Chem.* 2839 (2007)
195. M Zyder, T Szymańska-Buzar *J. Organomet. Chem.* **695** 1734 (2010)
196. M Zyder, T Szymańska-Buzar *J. Organomet. Chem.* **694** 2110 (2009)
197. M R Maddani, S K Moorthy, K R Prabhu *Tetrahedron* **66** 329 (2010)
198. E Keinan, D Perez *J. Org. Chem.* **52** 2576 (1987)
199. D Perez, N Greenspoon, E Keinan *J. Org. Chem.* **52** 5570 (1987)
200. T Schmidt *Tetrahedron Lett.* **35** 3513 (1994)
201. A C Fernandes, C C Romão *J. Mol. Catal. A: Chem.* **253** 96 (2006)
202. A C Fernandes, C C Romão *J. Mol. Catal. A: Chem.* **272** 60 (2007)
203. A C Fernandes, C C Romão *Tetrahedron Lett.* **46** 8881 (2005)
204. A C Fernandes, C C Romão *Tetrahedron Lett.* **48** 9176 (2007)
205. N A Kuz'mina, E Ts Chukovskaya, R Kh Freidlina *Dokl. Akad. Nauk SSSR* **254** 890 (1980); *Chem. Abstr.* **94** 65035 (1981)
206. N A Kuz'mina, N P Zhiryukhina, E Ts Chukovskaya, R Kh Freidlina *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **30** 1715 (1981)
207. R G Petrova, T D Churkina, I A Golikova, R Kh Freidlina *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **32** 1642 (1983)
208. R Kh Freidlina, R G Gasanov, N A Kuz'mina, E Ts Chukovskaya *Russ. Chem. Rev.* **54** 662 (1985)
209. H Firouzabadi, A Jamalian *Phosphorus, Sulfur, Silicon. Relat. Elem.* **170** 211 (2001)
210. R Sanz, J Escribano, Y Fernández, R Aguado, M R Pedrosa, F J Arnáiz *Synlett* 1389 (2005)
211. R Sanz, J Escribano, M R Pedrosa, R Aguado, F J Arnáiz *Adv. Synth. Catal.* **349** 713 (2007)
212. P R Sridhar, K R Prabhu, S Chandrasekaran *J. Org. Chem.* **68** 5261 (2003)
213. H Alper, J E Prickett, S Wollowitz *J. Am. Chem. Soc.* **99** 4330 (1977)
214. A Inada, H Heimgartner, H Schmid *Tetrahedron Lett.* 2983 (1979)
215. H Alper, C P Mahatantila, F Einstein, A Willis *J. Am. Chem. Soc.* **106** 2708 (1984)
216. N Jeong, S J Lee, B Y Lee, Y K Chung *Tetrahedron Lett.* **34** 4027 (1993)
217. J L Kent, H Wan, K M Brummond *Tetrahedron Lett.* **36** 2407 (1995)
218. K M Brummond, H Wan *Tetrahedron Lett.* **39** 931 (1998)
219. K M Brummond, H Wan, J L Kent *J. Org. Chem.* **63** 6535 (1998)
220. K M Brummond, A D Kerekes, H Wan *J. Org. Chem.* **67** 5156 (2002)
221. H Xiong, R P Hsung, L-L Wei, C R Berry, J A Mulder, B Stocwell *Org. Lett.* **2** 2869 (2000)
222. Q Shen, G B Hammond *J. Am. Chem. Soc.* **124** 6534 (2002)
223. H Cao, S G Van Ornum, J Deschamps, J Flippen-Anderson, F Laib, J M Cook *J. Am. Chem. Soc.* **127** 933 (2005)
224. F E McDonald, C C Schultz *J. Am. Chem. Soc.* **116** 9363 (1994)
225. N-F K Kaiser, A Hallberg, M Larhed *J. Comb. Chem.* **4** 109 (2002)
226. O Lagerlund, M Larhed *J. Comb. Chem.* **8** 4 (2006)
227. Y Wannberg, M Larhed *J. Org. Chem.* **68** 5750 (2003)
228. X Wu, J Wannberg, M Larhed *Tetrahedron* **62** 4665 (2006)
229. X Wu, M Larhed *Org. Lett.* **7** 3327 (2005)
230. X Wu, J K Ekegren, M Larhed *Organometallics* **25** 1434 (2006)
231. J Wannberg, N-F K Kaiser, L Vrang, B Samuelsson, M Larhed, A Hallberg *J. Comb. Chem.* **7** 611 (2005)
232. K Yamazaki, Y Kondo *J. Comb. Chem.* **6** 121 (2004)
233. Patent US 4654436 (1987); *Chem. Abstr.* **107** 6942 (1987)
234. P Appukkuttan, L Axelsson, E Van der Eycken, M Larhed *Tetrahedron Lett.* **49** 5625 (2008)
235. J Wannberg, Y A Sabnis, L Vrang, B Samuelsson, A Karlérn, A Hallberg, M Larhed *Bioorg. Med. Chem.* **14** 5303 (2006)
236. X Wu, R Rönn, T Gossas, M Larhed *J. Org. Chem.* **70** 3094 (2005)
237. J Georgsson, A Hallberg, M Larhed *J. Comb. Chem.* **5** 350 (2003)
238. X Wu, A K Mahalingam, Y Wan, M Alterman *Tetrahedron Lett.* **45** 4635 (2004)
239. X Wu, P Nilsson, M Larhed *J. Org. Chem.* **70** 346 (2005)
240. M Maddani, K R Prabhu *Terahedron Lett.* **48** 7151 (2007)
241. T Hirao, S Nagata, M Yamaguchi, Y Ohshiro *Bull. Chem. Soc. Jpn.* **64** 1713 (1991)
242. Y Mori, J Tsuji *Tetrahedron* **27** 3811 (1971)
243. C-T Chen, J-H Kuo, V D Pawar, Y S Munot, S-S Weng, C-H Ku, C-Y Liu *J. Org. Chem.* **70** 1188 (2005)
244. S Goswami, A C Maity *Tetrahedron Lett.* **49** 3092 (2008)
245. A Sakakura, S Umemura, R Kondo, K Ishihara *Adv. Synth. Catal.* **349** 551 (2007)
246. J Anderson-McKay, G P Savage, G W Simpson *Aust. J. Chem.* **49** 163 (1996)
247. M Nitta, T Kobayashi *J. Chem. Soc., Chem. Commun.* 877 (1982)
248. M Nitta, T Kobayashi *J. Chem. Soc., Perkin Trans 1* 1401 (1985)
249. P G Baraldi, A Barco, S Benetti, M Guarneri, S Manfredini, G P Pollini, D Simoni *Tetrahedron Lett.* **26** 5319 (1985)
250. P G Baraldi, A Barco, S Benetti, S Manfredini, D Simoni *Synthesis* 276 (1987)
251. M Nitta, A Yi, T Kobayashi *Bull. Chem. Soc. Jpn.* **58** 991 (1985)
252. C Hippeli, R Zimmer, H-U Reißig *Lieb. Ann. Chem.* 469 (1990)
253. R Zimmer, H-U Reissig *J. Org. Chem.* **57** 339 (1992)
254. K Alagiri, P Devadig, K R Prabhu *Tetrahedron Lett.* **53** 1456 (2012)
255. R I Khusnutdinov, N A Shchadneva, Yu Yu Mayakova, T M Oshnyakova, U M Dzhemilev *Russ. Chem. Bull. Int. Ed.* **62** 683 (2013)
256. S Cicchi, A Goti, A Brandi, A Guarna, F De Sarlo *Tetrahedron Lett.* **31** 3351 (1990)
257. B M Trost, J Yoshida, M Lautens *J. Am. Chem. Soc.* **105** 4494 (1983)